Közlemények a Szegedi Tudományegyetem Ásvány-Kőzettani Intézetéből.
Igazgató: Dr. KOCH SÁNDOR.
Publications of the Mineralogical Petrographical Institute of the University of Szeged (Hungary).

MINERALS FROM GYÖNGYÖSOROSZI[1]

BY S. KOCH

In the most important coloured metal-ore mining district of Hungary, in Gyöngyösoroszi, in the country of Heves and to the north of this village, the ore lodes extend over an area limited by andesite inclusions in an exposed older pyroxene andesite agglomerate. The greater part of the lodes fill up longitudinal, the smaller part, transversed fissure-systems, most of the latter are already in the andesite area of the Mátra Mountains. The lodes are predominantly filled up by different kinds of quartz, the longitudinal lodes show owing to their rhythmical separation a partly cryptocrystalline, striated structure, whilst the transversed lodes are filled with coarsely crystalline quartz often exhibiting a brecciated structure. So far, it only seemed worthwhile to operate the lodes filled with striated quartz as merely they contain ore. The minerals described below were mainly found in the principal lode, the Károly lode and the Péter-Pál one.

Until quite recently only investigations were carried out in Gyöngyösoroszi, the exposure of the lodes actually only began when the adit was opened up. Now there is also more exposing than productive work, thus it is not surprising that the literature dealing with the minerals of the deposite is still very incomplete. From the geological and mining-geological point of view P. Rozlozsnik[1] and G. Pantó[2, 3], from the mineral one F. Papp[4], K. Sztrókay[5, 6, 7], as well as Koch—Mezősi—Grasselly[8] dealt with the subject.

The dominating ore mineral of the ore lodes is sphalerite, beside it galena can be found in considerable amounts. It is interesting, that among the ores of the Károly lode ZnS occurs not only as sphalerite, but also as wurtzite.

Wurtzite forms at lower temperature from solutions of acid character therefore, it occurs far less frequently among the primar ore lode minerals than sphalerite which forms from the only quite mildly acid or even alkaline solutions, over wide temperature ranges. If wurtzite can be found it can usually be observed among the most recently formed sulphide ores in the form of needle crystal aggregates and very rarely as individual overgrown small crystals. The latter are mostly sphalerite paramorphoses after wurtzite. In the oxidation zone owing to the action of acid solutions sometimes wurztzite crystal groups and sometimes single small crystals can be found. *In Gyöngyösoroszi wurtzite belongs to the primarily formed sulphide ores.* Separate crystals could not be detected, they did not either

[1] Delivered as a lecture to the Geochemical Commission of the Hungarian Academy of Science at its Meeting in April 1954.

appear as »Schalenblende«, but as radial fanlike one cm long crystal groups attaining forming bands ingrown in quartz or band rows separated by thin quartz layers (Microphot. 1. and 2.). Its colour is clove brown, its lustre half metallic.

Considering that wurtzite and sphalerite are difficult to differenciate under the microscope thin sections of the ore were also prepared. In which the wurtzite crystal bundles were sometimes pointed and sometimes blunt, pyramidelike, transparent showing lighter or darker brownish-yellow colour. The colour changed from zone to zone depending on the amount of FeS. The cleavage according to (0001) could be observed on every sample examined. On certain points the crystal groups were quite free from inclusions; however, frequent by chalcopyrite inclusion rows extending along the boundaries of the crystal groups can be seen, on which dense chalcopyrite inclusion rows (Microphot. 3, 4 and 5) occur nearly perpendicularly, forming parallel with the cleavage plane usually rendering the wurtzite crystal group quite opaque. The substance of the chalcopyrite laths formed alternately with the wurtzite and intergrew with it in an oriented manner. In sections under the microscope with an oil immersion these orientally separated very abundant chalcopyrite inclusion rows running parallel with the cleavage plane can be well detected (Microphot. 6). Besides several of these micron sized inclusions wurtzite also contains oriented chalcopyrite sphenoid inclusions (Microphot. 7). As can be seen on microphoto No. 8. these sphenoids are the remnants of the chalcopyrite replaced by wurtzite.

Between crossed nicols the wurtzite crystals exhibit an anisotrope character showing an interference in the diagonal position. Optically they have a positive character. Thus it is beyond doubt that wurtzite and not a paramorph after wurtzite are involved. Even the light coloured crystals and crystals groups did not transform into sphalerite, although according to Ehrenberg the latter transform more rapidly than the dark coloured crystals containing much iron.

It is very interesting that on the (0001) plane of the wurtzite crystal groups sphalerite tetrahedrons overgrowing in an oriented manner can be found, i. e. tetrahedrons which sometimes do not contain any inclusions and others containing many chalcopyrite inclusions and even chalcopyrite sphenoids intergrown orientally with sphalerite (Microphot. 9 and 10). The most interesting sample is that on which on the (0001) plane of the wurtzite crystal group larger, incompletely developed sphalerite tetrahedrons are overgrown parallel whilst on the top of the sample a tetrahedron can be seen. The entire crystal group like most of our wurtzite crystal groups is embedded in quartz (Microphot. 11).

On the basis of its cleavage directions and owing to its isotropic character sphalerite can always be distinctly distinguished from wurtzite. Sometimes the sphalerite is lighter containing less dissolved FeS and sometimes darker than wurtzite. A remarkable section is that on which the fanlike wurtzite crystal group containing a large amount of FeS are overgrown as light sphalerite (Microphot. 12). In the interior of the sphalerite crystals associated with wurtzite the parts containing more and those containing less iron alternate in zones (Microphot. 13).

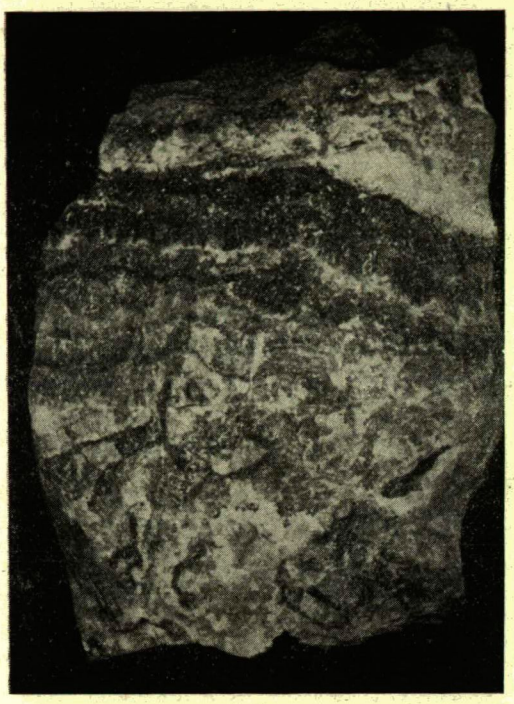


Fig. 1.
Lode fragment with wurtzite
about 1/3 the original size

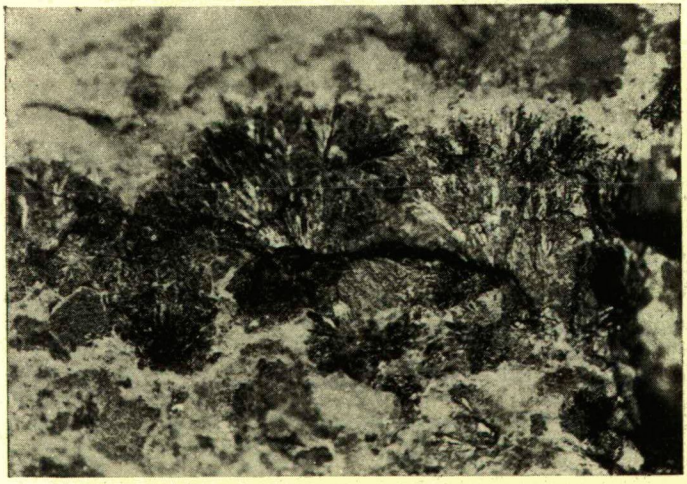


Fig. 2.
Lode fragment with wurtzite, × 4

Fig. 3.
Zonal wurtzite with chalcopyrite inclusions, × 40

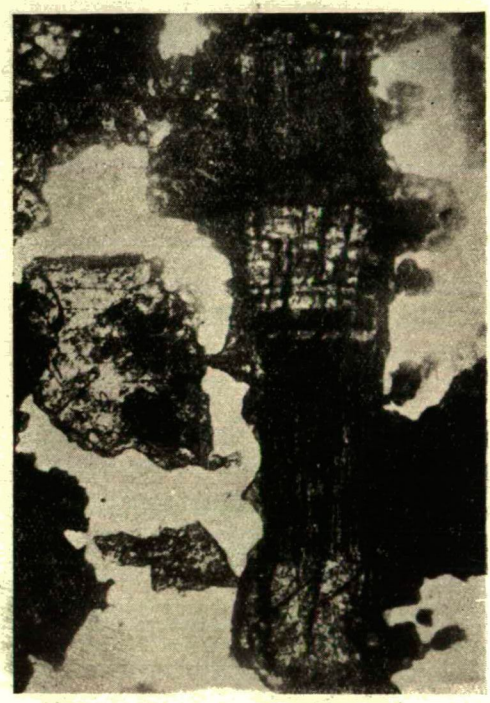


Fig. 4.
Wurtzite, with the 0001 plane parallel and to it perpendicular oriented chalcopyrite inclusion rows, × 90

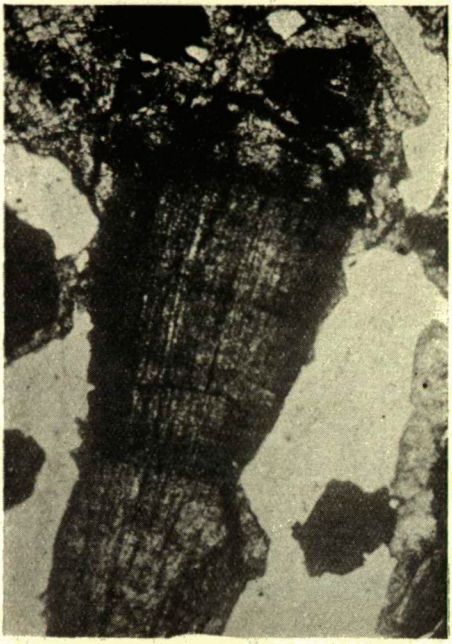


Fig. 5.
Zonal wurtzite, the section parallel to the *c* axis, × 110

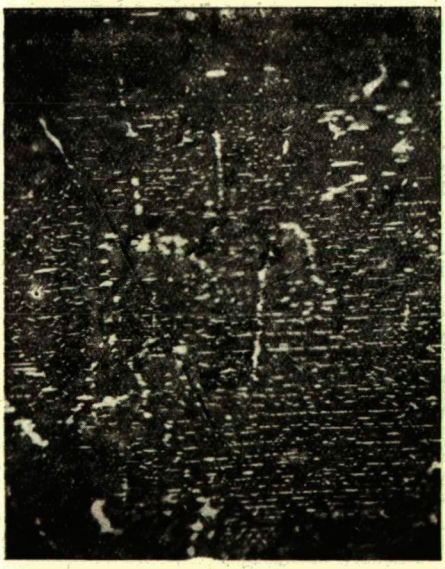


Fig. 6.
Wurtzite, chalcopyrite inclusion rows settled parallel with 0001, × 400

Fig. 7.
Wurtzite with oriented chalcopyrite sphenoids, × 50

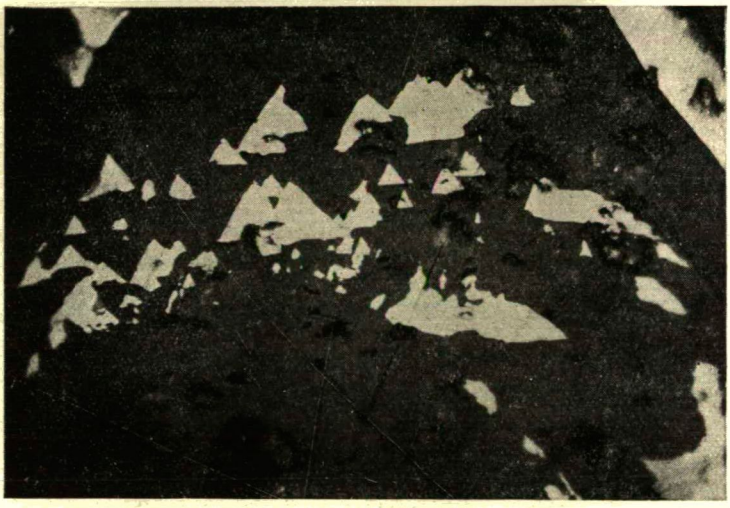


Fig. 8.
Sphalerite replacing chalcopyrite along sphenoid planes, × 250

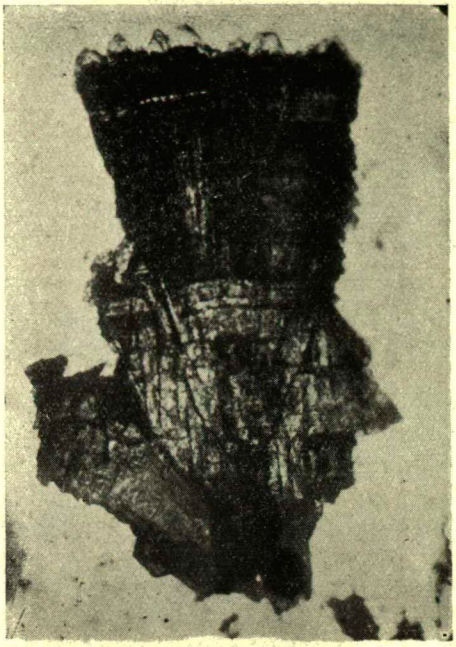


Fig. 9.
Zonal wurtzite crystal bundle, on the plane 0001 with sphalerite tetrahedrons, × 110

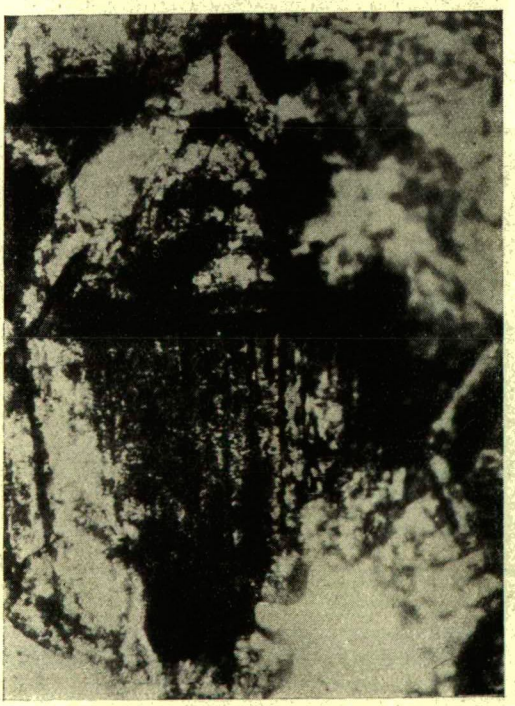


Fig. 10. Wurtzite, with sphalerite tetrahedron, × 150

Fig. 11.
Wurtzite crystal bundle with oriented overgrown sphalerite, × 140

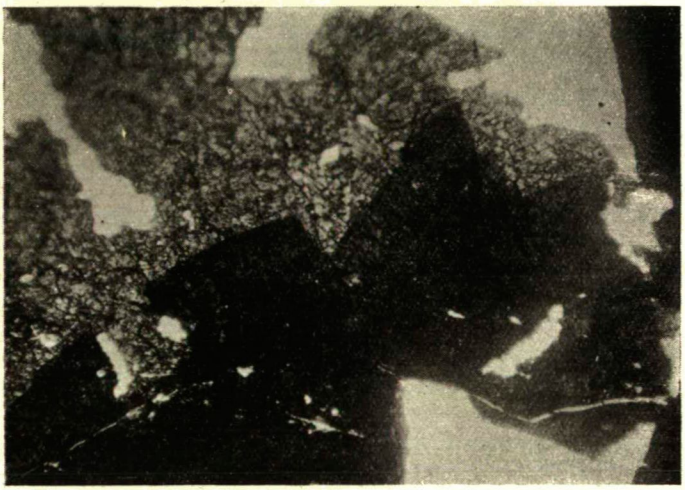


Fig. 12.
Wurtzite rich in iron (dark) with iron-poor sphalerite (gray), × 100

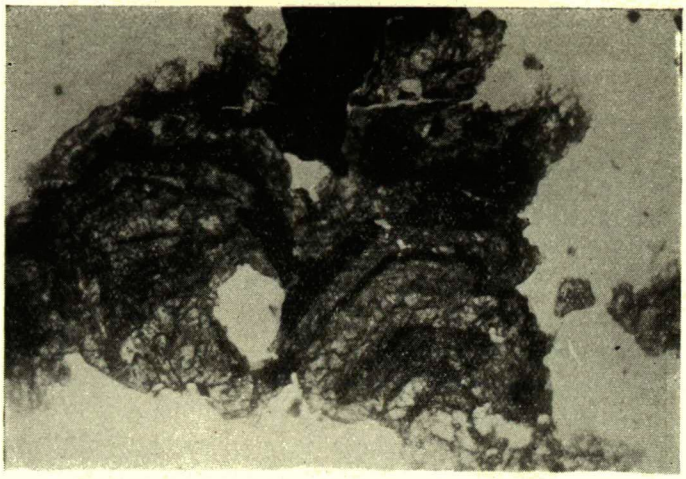


Fig. 13.
Zonal sphalerite, × 90

From the fragments from which thin sections were prepared polished sections were also made. The latter confirmed all observations made on the thin sections. On the wurtzite crystal groups the chalcopyrite inclusion rows extending along the single crystals forming fanlike not extensive branches, as well as the inclusion rows running parallel to the (0001) cleavage plane in an almost perpendicular direction to the former, can be well detected. The latter as shown on Microphot. 6. succeed each other in particularly dense rows. In the sphalerite crystal groups intergrown parallel to the wurtzite crystal ones the inclusion system formed regularly but in a manner diverging from that of the wurtzite is very conspicious. The shape of the sphalerite tetrahedrons can always easily be distinguished on the basis of the inclusions above wurtzite crystal group (Microphot. 14 and 15). Here it is also immediately plausible that not dismixture of the sphalerite-chalcopyrite system, but an oriented mineral intergrowth of two, with the wurtzite three, minerals is involved. An interesting polished section is that in which the wurtzite and the sphalerite orientally intergrown with it mostly do not contain inclusions, whereas the crystal group is limited by a chalcopyrite inclusion system running parallel with the cleavage plane (Microphot. 16). In this case also the shape of the sphalerite tetrahedron growing orientally, the inclusion row extending on the mutual (0001) (111) plane is very cleanly detectable. The crystal group surrounded by the chalcopyrite continued to develop and after a time another chalcopyrite inclusion system encircled it, a phantom crystal formed.

Besides the sections running parallel, or almost parallel, to the c axis others perpendicular to it were also prepared. The cross-section is a hexagon in which the parts containing more, and those containing less chalcopyrite inclusions alternate zonally (Microphot. 17). This zonal distribution of the inclusions can also be well detected in the polished sec-

tions. If the section was prepared obliquely to the *c* axis the hexagon was distorted (Microphot. 18, 19 and 20).

The two crystallised variations of ZnS can only occur beside each other under certain, definite, physico-chemical conditions according to A l l e n and C r e n s h a w, only if the solution contains at a temperature of 330—220°C 4—0.1 per cent of sulphuric acid. When the acid content is higher and the temperature is lower wurtzite, when the former is lower and the latter is higher sphalerite crystals form. It is not probable that our solutions contained any free sulphuric acid, however, it may be assumed that HF was the cause of the acid character of the solution. This

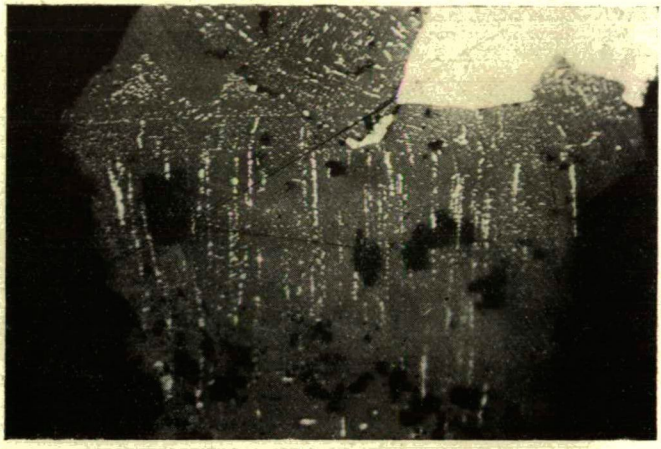


Fig. 14.
Wurtzite-sphalerite in oriented intergrowth, × 400

Fig. 15.
Wurtzite-sphalerite in oriented intergrowth, × 420

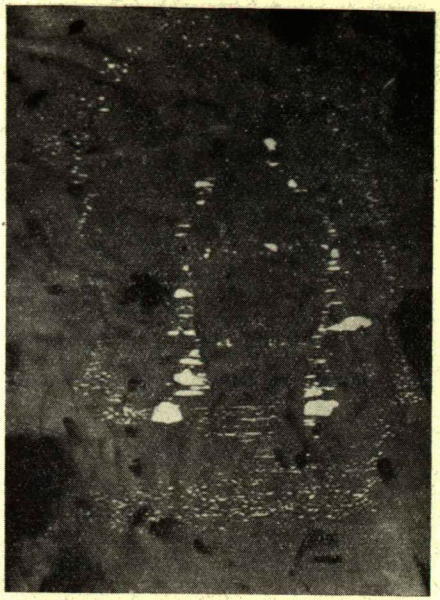


Fig. 16.
Wurtzite-sphalerite with chalcopyrite border, × 450

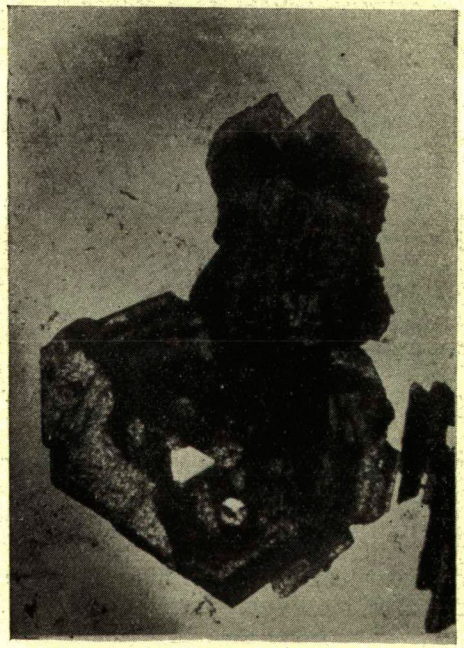


Fig. 17.
Wurtzite crystal groups parallel and perpendicular, respectively to the vertical axis, with oriented chalcopyrite inclusions, × 110

Fig. 18.
Zonal wurtzite, parallel to the plane 0001, × 450

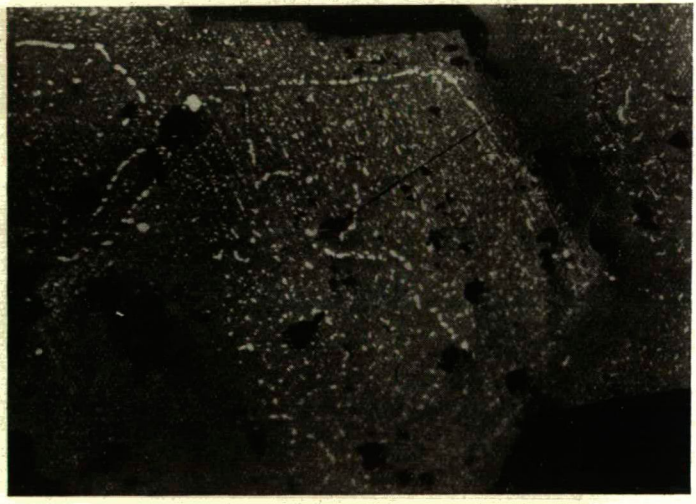


Fig. 19.
Zonal wurtzite, parallel to the plane 0001, × 340

suggestion is supported by the fact that in the younger crystalline quartz, surrounding the ores, very well developed small fluorite crystals, octahedrons, octahedral crystal groups were found as inclusions (Microphot. 21). These crystal groups were sometimes deposited on wurtzite (Microphot. 22) and sometimes on the older galena replaced by the quartz (Microphot. 23). The row of fluorite crystal inclusions (Microphot. 24) following the lines of the quartz crystal growth which are enclosed by the growing quartz crystals is very fine. Considering that the free acid content of the solution is not known wide limits ranging between 330—220°C must be

set for the beginning of the ore-forming probably, however, it occurs in the vicinity of the lower temperature ranges. Consequently the ore formation began in the mesothermal period. When, owing to the formation of fluorite, the free acid content of the solution vanished the separation of wurtzite ceased, among the younger ores forming at lower temperatures this mineral can no more be found.

Wurtzite is not a wide distributed mineral of Gyöngyösoroszi, so far it was only found at some points of the main lode, the Károly lode. It is more or less frequently associated with intergrown fluorite crystal microscopi-

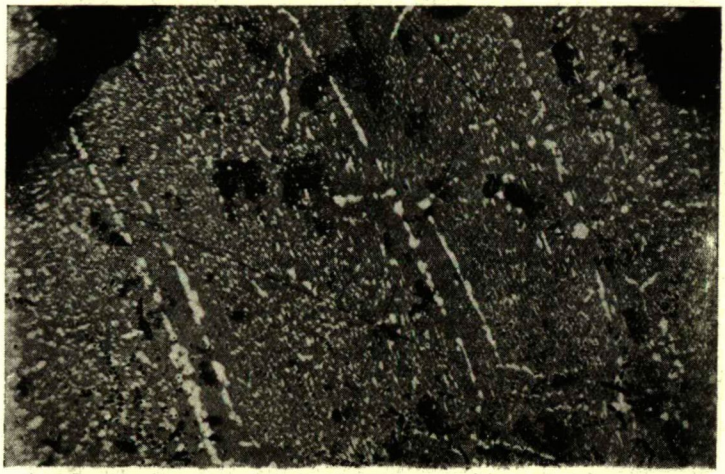


Fig. 20.
Oriented intergrowth of wurtzite and chalcopyrite, × 500

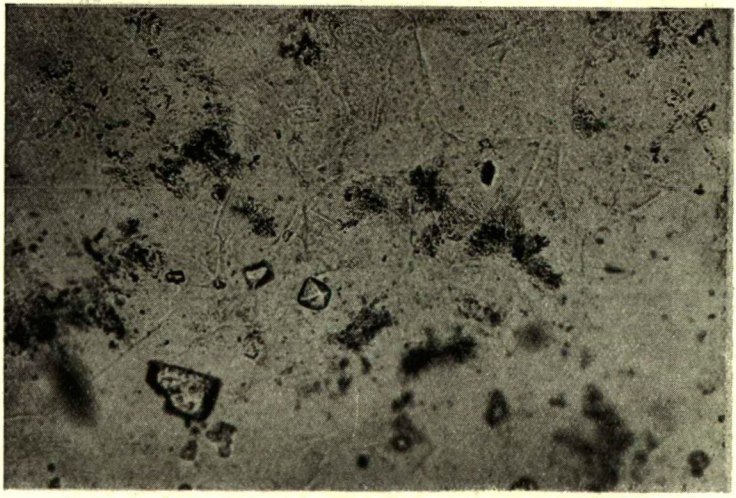


Fig. 21.
Fluorite crystals in quartz, × 170

cally small in size. Moreover fluorite cannot only be detected among the lodes, but also fairly abundantly[8] among the minerals of the cavities of the tufaceous agglomerates and the amygdaloidic andesite minerals of the adit indicating that a considerable amount of the HF contained in the residual solution was already bound before the formation of the ore lodes.

Where the residual solution did not contain fluorine acid the first generation of ZnS separated as black coloured sphalerite containing a

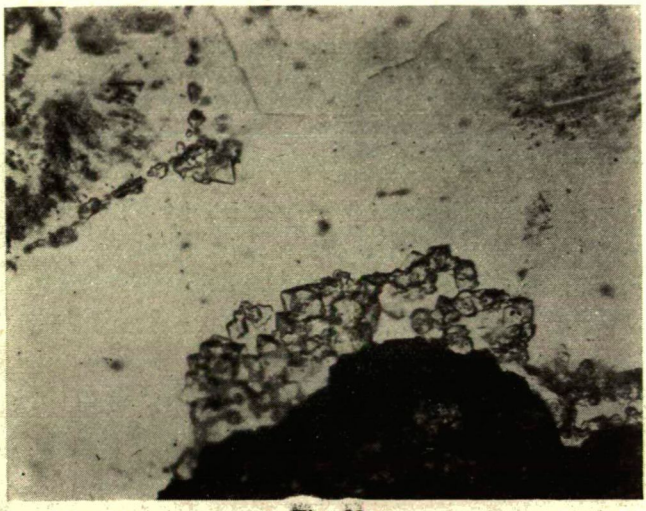


Fig. 22.
Fluorite crystals on wurtzite, × 170

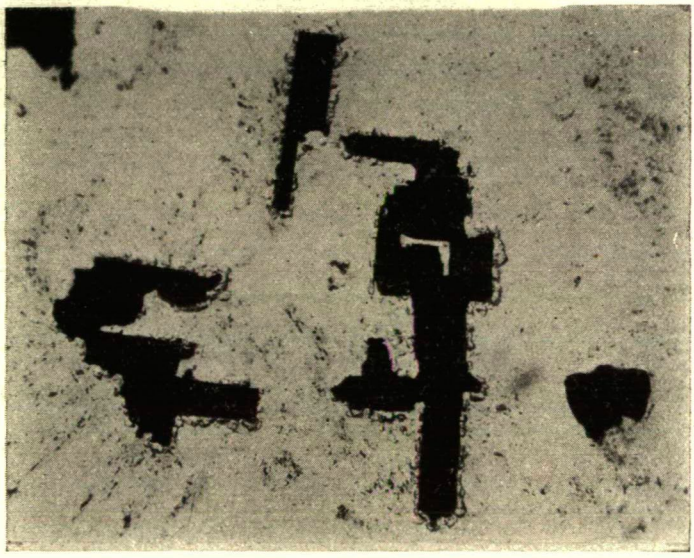


Fig. 23.
Fluorite crystals on galena replaced by quartz, × 125

large amount of iron and many chalcopyrite inclusions. Under the microscope it shows reddish-brownish internal reflexes. Undoubtedly the inclusions are partly the product of dismixture, however, the two ores can also be found separating rhythmically, the coherent chalcopyrite rows overgrow it orientally and change according to the substance of the sphalerite crystal (Microphot. 25). However, the overwhelming majority of the inclusi-

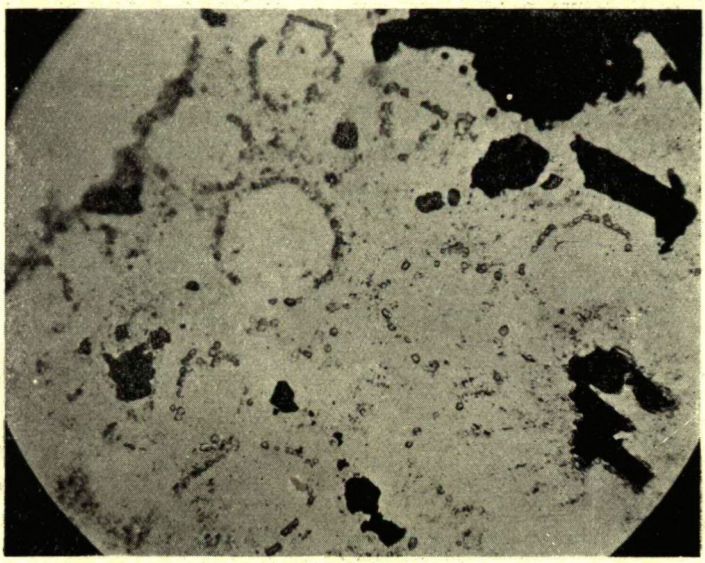


Fig. 24.
Fluorite crystals oriented along the periphery of quartz crystals, × 80

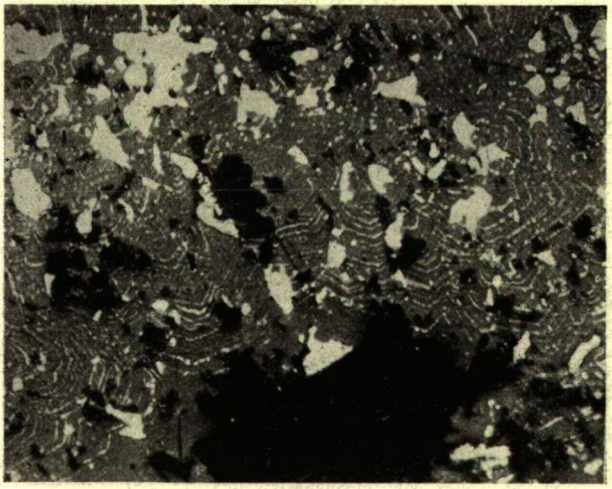


Fig. 25.
Rhythmically oriented separation of sphalerite and chalcopyrite, × 250

ons are chalcopyrite fragments replaced by the recrystallised sphalerite. The remnants of the original ore can sometimes be found regularly, and sometimes quite irregularly localised in the sphalerite surrounding, and at the same time, replacing it (Microphot. 26, 27). In the former case the differently orientated original chalcopyrite granule boundaries (Microphot. 27) can be reconstructed. Around the larger chalcopyrite islands the replacing sphalerite very frequently contains oriented chalcopyrite

Fig 26.
Sphalerite replacing chalcopyrite, × 340

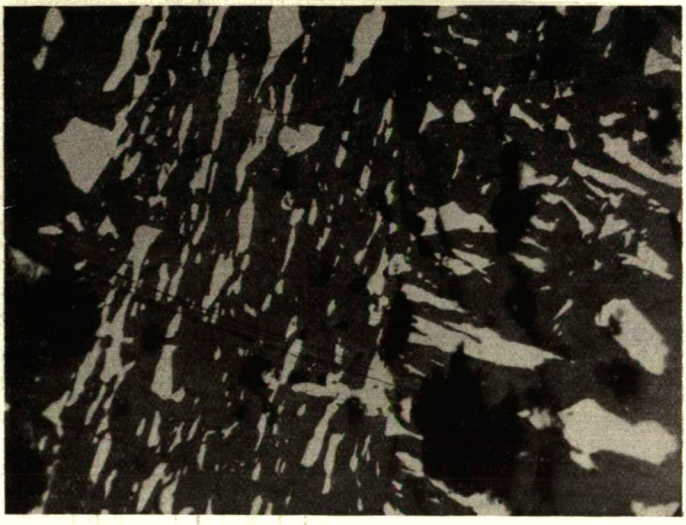


Fig. 27.
Sphalerite replacing chalcopyrite, × 260

inclusion rows which can only be well detected in oil immersion, these also represent remnants of the replaced chalcopyrite.

Besides the chalcopyrite older than the sphalerite by which it is replaced and that formed simultaneously with the sphalerite which separated rhythmically with it, the older sphalerites which are rich in iron also contain younger chalcopyrite. This chalcopyrite permeates in thin veins taking an irregular course and widening at some places the sphalerite probably following the fissures of the ore resulting from tectonic effects. In these chalcopyrite ores the ore sometimes alternates with stannite. The grey ore possessing a relatively weak reflection capacity did not show pleochroism, but between crossed nicols the interference phenomenon can be detected. By means of the spectroscope the stannum contained in the black sphalerite to which it is bound is well visible (Microphot. 28).

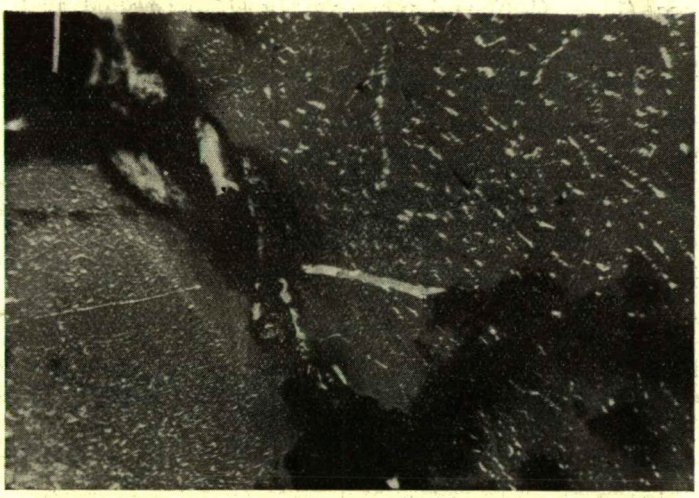


Fig. 28.
Stannite with chalcopyrite, × 500

Apart from chalcopyrite, both wurtzite and sphalerite, often also contain remnants of the older galena replaced by them. Microphot. 25 illustrates well the galena remnants replaced by the two rhythmically separated ores sphalerite and chalcopyrite. It seems very likely that after pyrite, the strongly corroded remnants of which can be observed in all so far mentioned ores, the first galena generation separated, however, the greater part of this galena was replaced by chalcopyrite and sphalerite (wurtzite). These sulphide ores formed at higher temperatures only in small amounts were replaced by quartz which separated in great masses. The replacement followed the cleavage planes of the sulphides.

Hence, at higher temperatures only small amounts of ore separate therefore in many of the hitherto exposed ore lode sections, they cannot be found only later, after the temperature of the solution decreased ores formed in larger quantities.

Sphalerite which separated as second generation is the dominating ore of the lodes, it has a brownish-yellow colour and its iron content

is appreciably lower than that of the former. This sphalerite composes with galena and with very little or no chalcopyrite, either coarsely granular groups in thinner or thicker cords in quartzous gangue or the sphalerite is ingrown as scattered rounded rhombohedral shaped grains in quartz and calcite respectively. Among these intergrown crystals those showing a zonal structure are frequent, the younger layers can be separated from the somewhat darker coloured nucleus. This sphalerite, which is younger and contains less iron than that described above exhibits under the microscope a light, yellowish-brownish, internal reflex having far less chalcopyrite inclusions, these occurring in it are chalcopyrite remnants replaced by sphalerite.

Its little crystals, less than one cm in size, can often be found in smaller cavities overgrown on quartz, planes (111) dominate on them, besides them planes ($11\bar{1}$), (100) and more rarely (110) as well as (311) can be detected the latter shape is incompletely developed and has only a few planes. The greater part of the crystals are twins. The angular rubble sphalerite contained in the quartz of the brecciated ore frequently occurring in the Károly lode fell into fragments at the crystallisation of the large amounts of silicic acid which had separated in the gel state.

The chemical analyses of wurtzite (I), the black, older sphalerite (II) and the quantitatively dominating lighter young sphalerite (III) yielded the following results:

	I. a.	I. b.	II.	III. a.	III. b.
Zn	29,71 %	42,99 %	55,87 %	46,54 %	59,78 %
Cd	0,11	not determ.	0,48	0,29	not determ.
Fe	3,12	6,52	3,85	1,92	2,58
Mn	0,15	trace	0,10	0,10	0,69
Cu	0,62	0,78	0,31	0,07	0,10
Pb	9,73	10,77	3,95	4,03	1,66
As	—	—	—	trace	trace
S	18,30	26,96	31,21	24,72	32,87
SiO_2	37,75	12,54	3,89	21,84	1,72
	99,47 %	100,56 %	99,66 %	99,51 %	99,40 %

Subtracting the insoluble SiO_2 and calculating the sulphide residual for 100 per cent the following results are obtained:

	I. a.	I. b.	II.	III. a.	III. b.
Zn	48,14 %	48,86 %	58,35 %	59,94 %	61,21 %
Cd	0,17	—	0,50	0,37	—
Fe	5,05	7,40	4,02	2,47	2,64
Mn	0,24	—	0,10	0,12	0,70
Cu	1,00	0,88	0,32	0,09	0,10
Pb	15,75	12,23	4,12	5,18	1,69
S	29,65	30,63	32,59	31,83	33,66
	100,00 %	100,00 %	100,00 %	100,00 %	100,00 %

Besides these trace elements which could also be identified by means of chemical analyses the spectroscopical examination still showed the following:

Ag in all three samples, in the following intensity sequel: II., III., I.

Sn in all three samples, in the following intensity sequel: II., far weaker III, I.

Considering that also under the microscope stannine could only be detected in the older sphalerite, marked with II., the results of the spectroscopical investigation are in this case too in good agreement with our observations.

The younger, light, sphalerite fluoresces with a nice dark violet colour, on the action of ultraviolet rays. In the case of dark sphalerite and wurtzite, owing to their high iron content, the fluorescence phenomenon is very slight or fails to occur.

The first generation of the other dominating ore of the lodes, galena, is as already mentioned partly older than wurtzite and black sphalerite. Its amount is also in this case insignificant, the two variation of ZnS and quartz replace it. Both wurtzite and the older sphalerite very frequently contain larger or smaller galena remnants showing already partly advanced replacement, this explains why the two zinc ores always contain lead in considerable amounts. (Microphot. 29). On chalcographical etching this older galena showed a nice zonal structure. In two sections of these galena remnants replaced by the older sphalerite very tiny gold grains, several microns in size, could be detected. (Microphot. 30). Consequently, the separation of gold began simultaneously with the formation of the sulphide ore. The older galena also already contains bournonite in small patches it is, however, far rarer in this ore than in the dominating younger galena.

Fig. 29.

Sphalerite replacing galena with chalcopyrite inclusion rows of the same age than the latter, × 170

The latter associated with light sphalerite is one of the main ores of the mining district, it occurs in the gangue in dispersed granules or as independent thinner veins composing smaller nests, in the latter case it forms coarsely granular, or radial-crystalline masses. In the polished sections prepared from this galena parallel dot rows due to the strikingly fine mother liquor inclusion mentioned by Sztrókay are frequent. The separation of galena began before that of the younger sphalerite — this

Fig. 30.
Gold in galena replaced by sphalerite, × 300

fact has also been established by Sztrókay — the sphalerite contains remnants of the galena displaced by it, hence it also contains lead in considerable amounts, whereas the large zinc content of galena (s. analysis) is due to the sphalerite replacing it developing along the mother liquor inclusions mentioned above.

In the smaller cavities very fine overgrown galena crystals can be found. The crystals are usually combinations of planes (111) and (100) the former is the dominating one, the latter blunts the peaks of the former, less frequently small hexahedrons also occur. A small galena crystal ingrown in granular calcite is apparently a hexagon tabular is a deficiently developed contact twin which flattened according to one of the axis of the trigonal symmetry of the two cube-octahedrons developed in equilibrium.

The galena is replaced by sphalerite, chalcopyrite, and by the bournonite formed at expense of the substance of the galena, as well as by the jamesonite and semseyite. The granules of bournonite are always arranged in very fine twin lamellae they occur fairly frequently. This mineral was also found in small overgrown twin crystals. The crystals are about one mm in size and are overgrown on quartz. Jamesonite needle aggregates appear at the borders of the galena, sometimes the jameso-

nite formed at the expense of the galena completely surrounds some single galena granule. A fanlike crystal group overgrown at the edge of a small galena crystal in the brecciated ore also occurred, on the basis of its reflection and interference we identified it as semseyite. In the younger galena gold could not be found, neither could the boulangerite mentioned by Sztrókay, nor the miargyrite marked by him with note of interrogation be identified. In all sections traces of a commencing decomposition of the galena could be observed it is permeated by thin cerussite veins containing one or more covellite plates. The result of the analyses of the younger galena are as follows:

	I.	II.
Pb	71,54 %	75,42 %
Zn	0,64	7,69
Fe	0,91	0,12
Cu	trace	0,75
Mn	trace	—
Sb	0,20	0,48
S	16,92	15,51
SiO_2	0,45	0,25
	99,66 %	100,22 %

The material for the analyses was taken from a coarsely radial pure small galena lode. The Sb content is due to the not negligable lead-antimony sulphides.

The third, less frequent, ore of the mining district is chalcopyrite also occurring in two generations an older and a younger one. It always can only be detected as small granules or patches, it has not yet been found as a coherent lode filling, like sphalerite or galena. It is partly older than sphalerite and partly it separated at the same time as the latter. It frequently contains badly corroded granules of the older pyrite. The polished sections of chalcopyrite always exhibited between crossed nicols a twin lamellae structure even the electrographically etched granules showed a very thin polysynthetic twin lamellae structure. Intergrown in the quartz of the lode scattered, well developed, sphenodic small crystals also occur, whilst more recently larger overgrown curved sphenoidic crystals with blurred planes could be observed in the southern lodes of Hidegkut 2 and also in those of Kőkut. At the edge of the chalcopyrite granules in some of the polished sections a thin chalcocite band containing small covellite lamellae occurred.

Among the sulphide ores crystals of pyrite were the first to separate. Their intergrown hexahedral crystals can already frequently be seen in the accessory rocks and also at the edges of the lodes which are in contact with the latter. In the first generation of all sulphide ores the strongly resorbed remnants of these crystals can always be formed. The second pyrite generatio consists of small compact granules it does not

occur in the Károly lode in larger masses or as independent nests, as thin cords in dispersed patches, however, it is not infrequent. It encrusts sphalerite, quartz and calcite and can be found overgrown on them as small hexahedral, pentagonal dodecahedral crystals or crystal groups. In the calcite filling of the Károly lode compact, quite gellike pyrite, forms veins attaining one cm in size which often limit the light coloured calcite from the brown- dark brownish one stained by MnO_2 [2]. The interior of the pyrite exhibiting a gel structure, patchings shining in bright interference colours often can be found. Sztrókay assumes that these more compact small granules which are easier to polish than the gellike pyrite are, owing to their As or Sb content, pyrite granules exhibiting an anomalic optical character, in the view of the author they are marcasite crystals. The more so as marcasite occurs extensively in our mining district. Its crystal aggregates with their fine twin crystals can often be detected in our sections. It represents an interesting phenomenon when its thin needle crystals are overgrown on idiomorphous hexahedral pyrite crystals, quasi forming a frame around them.

On overgrown sphalerite crystals arsenopyrite crystals hardly one mm in size surrounded by planes (110), (001) and (101) occurred. Our sections did not show this ore.

Not taking quartz and its varieties, which can now be found in dominating amounts in this mining district, furthermore calcite, also occurring in large amounts, into consideration only laumontite and cerussite observed as secondary minerals will still be mentioned.

Laumontite was detected on overgrown small quartz crystals clear as water at the 600th m of the adit. On the small crystals 2—4 mm in size we succeeded in establishing besides the dominating (110) planes still those of (111) and (001).

Small cerussite crystals were found in the hollows of a sphalerite pyrite samples. On the crystals as clear as water the following forms could be observed: (001), (010), (110) and (021). They are slightly alongated hexagonal tabular shaped crystals with the dominating base.

According to our grouping the following minerals could so far be observed at Gyöngyösoroszi:

Ores: pyrite I, galena I, gold, chalcopyrite I, sphalerite I, wurtzite, stannite, bournonite, *galena II, sphalerite II,* chalcopyrite II, marcasite, pyrite II, jamesonite, semseyite, arsenopyrite, tetrahedrite, antimonite.

(We did not succeeded in finding the boulangerite and miargyrite mentioned by Sztrókay.)

Non ore minerals: *quartzvarieties* (quartzite, chalcedony, jasper, rock crystal, amethyst), opal, *calcite,* dolomite, fluorite, pennine, barite, coelestite, gypsum I, laumontite. Among the minerals of the tufaceous agglomerate: adularia.

The minerals of the oxidized zone: chalcocite, covellite, cerussite, sulphur, gypsum II.

The chemical elements taking part in the formation of the minerals of the ore lodes: *O Si Ca S C Fe Zn Pb* Mn Mg Cu H F Cd Ba Al Sr P K As Ag Au.

Ooccurring in traces which can only be detected spectroscopically Sn Mo.

SUMMARY:

1. The substance of the residual solution containing large amounts of silicic acid separated in the older longitudional ore lodes rhythmically, but coherently. The smaller part of the separated material is of mezo-, the greater part of epithermal origin. The silicic acid separating as gel and crystallising slowly partly broke up the earlier crystallised ore embedding its fragments and partly displacing it. 2. The longitudional ore lodes belong to the row of the zinc lead ore lodes (Selmecbánya, Felsőbánya, Kapnikbánya etc.) which contain gold and silver and are wide distributed among the subvulcanic ore formations bound to the young tertiary mountain ranges, unfortunately, however, they are far less rich and do not resemble in anyway the ore occurrence of Nagybörzsöny.

The extremely variable crystals of calcite and crystallised quartz in which solid and liquid inclusions occur so abundantly seem worthy of further investigation.

Analyses and microphotographs by Gy. Grasselly.

REFERENCES:

1. Rozsloznik P. l: Adatok a gyöngyösoroszi környéki érctelérek ismeretéhez. (M. K. Földt. Int. Évi Jelentései az 1936—38. évekről. II. K. Budapest. 1942.)
2. Pantó Gábor: A gyöngyösoroszi magmadifferenciáció és ércképződés. (M. Tud. Akad. Műsz. Tud. Oszt. Közl. V. K. 129. o. 1952.)
3. Pantó Gábor: Bányaföldtani fölvétel Gyöngyösoroszin. (M. Áll. Földt. Int. Évi jelentése az 1950. évről. 1953. 155. o.)
4. Papp Ferenc: Ércvizsgálatok hazai előfordulásokon. (Földt. Közl. LXIII. 1953. 8. o.)
5. Sztrókay Kálmán: Néhány ásvány Gyöngyösoroszióból. (Földt. Közl. LXVIII. 1938. 30. o.)
6. Sztrókay Kálmán: A gyöngyösoroszi ~ ércelőfordulás mikroszkópi vizsgálata. (Math. Term. tud. Ért. LXIII. 1939. 904. o.)
7. Sztrókay Kálmán: Célesztin Gyöngyösoroszi ércteléreiből. (Földt. Közl. LXXXII. 1952. 304. o.)
8. Koch—Mezősi—Grasselly: A gyöngyösoroszi Zgyerka altáró kőzetei és ásványai. (Acta. Min. Petr. Tom. III. 1949. 1. o.)

THE HUNGARIAN MINERAL OCCURRENCES

PRELIMINARY REPORT

BY S. KOCH

C. Leonard[1], V. Schönbauer[2] and A. Zipser[3] elaborated merely topographically the areas of the Hungarian mineral occurrences. They began their work at the beginning of the XIXth century. It was continued in the second part of the century by E. Fellenberg[5], V. Zepharovich[4] and M. Tóth.[6] In their writing they mostly only mentioned the areas in which the mineral species, enumerated in an alphabetical order, occur. Zepharovich also reports a few crystallographic data. His very precise work has served until quite recently as book of reference for the authors of text-book and manuals.

When A. Semsey offered a grant of 100.000 Forints to the Hungarian Academy of Science under the condition that it will conduct a competition at the annual meeting in 1890 for ten different scientific branches which are of special interest in Hungary, writing entitled »the Minerals of Hungary« was also mentioned.

The latter was never written considering that the mineral domain of Hungary was so little known at the beginning of our century that a life time would not have been sufficient to fill up the gaps, particularly in a period in which personal jelousy was such a great obstacle to all kind of collective work.

The data available were for the most part topographic and crystallographic these scarce mosaics made the production of a uniform picture very difficult.

After the first two decades of this century a few crystallographic monographies (pyrites, calcites, cerussites) appeared, furthermore the genetical system[7] of mineral occurrences of Hungary was completed and the microscopical examination of the ore occurrences commenced.

After the liberation the work was in part collective, the mineralogic and geochemical writings filled up many gaps and furnished new data relating to our knowledge of the Hungarian mineral domain enabling the elaboration of the mineral corresponding to the niveau of up to date science. The outlines of this work which is in progress are presented below.

As has been established on the basis of geological construction and structure by E. Vadász[8] in Hungary basic mountain ranges, deck-mountains, botton-mountains and basin formations, the latter extend over

most of the area can be distinguished. Corresponding to this geological structure the useful Hungarian mineral occurrences of magmatic origin containing few minerals are sparse, from the geological point of view, however, they are very interesting. Among the sedimentary occurrences those which are the most important from the economic point of view are not involved in our sphere of interest as their components are bauxite, bentonite, and coal which are rocks. The mineral occurrences associated with them, e. g. gypsum from Gánt, alunite, ajkaite from Ajka etc.,* as well as the minerals contained in the magmatic rocks or tuffs respectively, however, as developed crystals and crystal aggregates which can be freed, like for example the minerals of the olivine bombs and the amphibol crystals of the basalt tuffs around Lake Balaton, the granates freed at the decomposition of the andesites of the Dunazug Mountains are already included. Of the less significant and very frequent calcite, pyrite occurrences only those are described which have at least been crystallographically elaborated.

At the enumeration of the mineral occurrences the combination of the chemical elements occurring in the minerals of the deposites are always reported.

I. OCCURRENCES OF MAGMATIC ORIGIN.

a) Protocrystallization.

Szarvaskő (Heves). In wherlite separated from gabbro of the Jurassic or lower Cretaceous period: olivine, magnetite, ilmenite, a small amount of hematite, pyrrhotite, pentlandite, valleriite, chalcopyrrhotite, pyrite, cubanite, chalcopyrite.

Secondarily: limonite, prehnite.

Combination of elements: O Fe Si Mg Ti Al Ca Na K V H P C S Cu

Spectrographically: Cr Ni Pt could be detected.

Somoskő (Nógrád): in the basalt of the Medves Mountains extruded at the end of the Pannonian (mine Eresztvény) titanomagnetite.

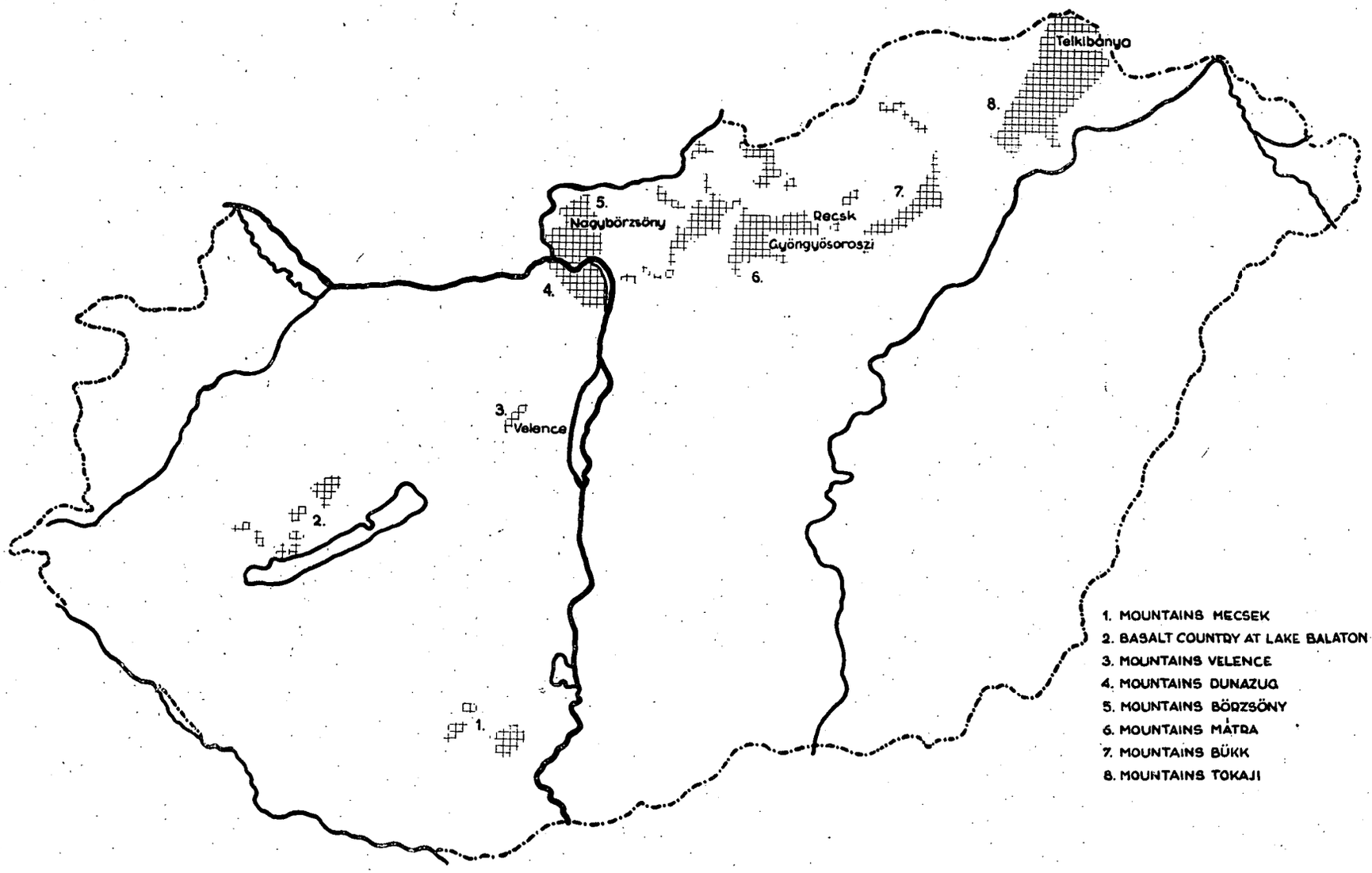
Mt. Gulács (Veszprém): in basalt derived from the same period pyrrhotite in drops exceeding 1 cm in size containing pentlandite, in which as dismixture valleriite, chalcopyrite, magnetite can be found.

b) Mesocrystallization.

Mt. Szentgyörgy, Bondoró, Magyargencs, Szentbékálla, Szigliget, Tihany, (all in Veszprém). Dobra, Szitke, (Vas): olivine bombs and olivine crystal aggregates in the tuffs of the basalt mentioned above.

Mindszentkálla, Balatoncsicsó (Veszprém), Tobaj (Vas), Balatonboglár (Somogy), Szilvaskő (Nógrád): amphibole crystals from the tuffs of the above basalt.

* The book of E. Szádeczky-Kardos — member of the Hungarian Academy of Science — entitled Szénkőzettan (Bp. 1952) deals in detail with the minerals of our coal mines.


Telkibánya
8.
5.
Nagybörzsöny
Recsk
Gyöngyösoroszi
7.
6.
4.
3.
Velence
2.
1.
1. MOUNTAINS MECSEK
2. BASALT COUNTRY AT LAKE BALATON
3. MOUNTAINS VELENCE
4. MOUNTAINS DUNAZUG
5. MOUNTAINS BÖRZSÖNY
6. MOUNTAINS MÁTRA
7. MOUNTAINS BÜKK
8. MOUNTAINS TOKAJI

Kapolcs (Veszprém): olivine, amphibole, biotite from basalt tuffs.

Somoskő (Nográd): olivine, augite from basalt of the Medves Mountains.

Börzsöny (Pest): augite, amphibole, garnet from the agglomerates of the andesite tuffs of the Miocene period of Csehvár and Mt. Magos.

c) Telocrystallization.

1. Autopneumatolytic.

Celldömölk (Vas) apatite, ilmenite, pyroxene, labradorite in the basalt cavities of Mt. Ság.

In the basalt cavities of Haláp (Veszprém): ilmenite, magnetite, augite, andesine, biotite.

Börzsöny Mountains (Pest): in the cavities of hyperstenandesite of the Miocene period of Nagyinóc: amphibole, biotite.

2. Contactpneumatolytic.

Magyaregregy (Baranya): magnetite, martite, hematite, pyrite formed on the contactpneumatolitical action of trachydolerite in the early Cretaceous period.

Secondarily: limonite, goethite.

In the vicinity of Pátka (Velence Mountains) magnetite in traces.

3. Pneumatolytic.

Tornaszentandrás (Borsód-Abaúj-Zemplén). In the ladiniceous limestone on the action of pneumatolytic natrongabbro of the Cretaceous period: hematite.

4. Pneumatolytic-hydrotermal.

Velence Mountains (Fejér) non-ore and ore minerals formed in the course of telocrystallization of the granite magma of the pre-Permian period: turmaline, topaz, molybdenite, pyrite, quartz, arsenopyrite, sphalerite, galena, chalcopyrite, hematite, fluorite, barite, antimonite, cinnabar.

Secondarily: cerussite, pyrolusite.

Combination of elements: O Si Ca F Ba S Fe Zn Pb Al C Na K Mg B Cu Mo Sb Hg H Mn Ag As Bi

Spectroscopically: Li Sn Ga Cd W U could be detected.

The minerals formed on the pneumatolytical-hydrotermal action of andesite magma of the Eocene period occuring in the quarry of Nadap: quartz, pyrite, hematite, sphalerite, epidote, fluorite, epistilbite, levyn, laumontite, heulandite, chabazite, desmine, scolecite, mesolite, barite, calcite.

Secondarily: gypsum.

5. Hydrothermalmetasomatic.

Szabadbattyán (Fehér). In the Carboniferous limestone of the Mt. Szár on the action of the residual solution of the granite magma of the Velence Mountains: galena, chalcopyrite, tetrahedrite, bournonite, quartz.

Secondarily: cerussite, anglesite, pyromorphite, covellite, copper, cuprite, azurite, malachite, calcite, dolomite.

The combination of the elements: Pb S Fe O Ca C Si Mg Cu P Sb Ag Zn H.

Rudabánya (Borsod). The minerals of the ore mass formed out of dolomite of the middle-Triassic period on the metasomatical action of residual solution of granite-magma: ankerite, siderite, quartz, barite, hematite, calcite, galena, pyrite, chalcopyrite, bornite, sphalerite, tetrahedrite, jamesonite, bournonite, pyrargyrite, gold.

Secondarily: limonite, hematite, pyrolusite, psilomelane, barite II, quartz II, redruthite, covellite, native copper, tenorite, cuprite, azurite, malachite, anglesite, cerussite, aragonite, cinnabar, mercury, pyrite II, marcasite, cacoxenite, calcite II, sulphur, gypsum.

The combination of the elements: O C Fe Ca Mg Si Ba S Al Mn H Cu Pb Zn Sb Hg Ag Au K Na Sr P.

Spectroscopically: Li B Ga can be detected.

Martonyi (Borsod): the minerals are of the same origin as those of Rudabánya: ankerite, quartz, barite, pyrite, chalcopyrite, bornite, tetrahedrite.

Secondarily: limonite, chalcosine, covellite, malachite, azurite. The combination of the elements: O C Ca Mg Fe Mn Si H Al Ba S Cu Sb Hg.

6. Hydrotermal.

Bajpatak (Heves). In the amygdaloid cavities of the diabaz lodes piercing the layers of the Triassic-period in the vicinity of Bajpatak in the Mátra Mountains: native copper, calcite.

Nagybörzsöny (Pest). The ore and non-ore associated minerals of the lodes formed at high temperatures bound to propylitized biotite amphibolandezites and dacites of the early Tertiary period: quartz, pyrrhotite, valleriite, pyrite I, molybdenite, sphalerite, galena, arsenopyrite, bornite, chalcopyrite, tetrahedrite, gold, bismuth, bismutine, galenobismuthite, cosalite, tetradymite, telluride of bismuth, csiklovaite, argentite, hessite, petzite, jamesonite, semseyite.

Secondarily: melnikovite, pyrite II, marcasite, siderite, magnetite, cronstedtite, redruthite, barite, quartz II, calcite, dolomite, goethite, arsenolite, limonite.

The combination of the elements: S Fe O Zn Si C Ca Pb Cu As Hg Mn Sb H Ba Ag Bi Co F P Au Te.

Spectroscopically: Cd Ni Mo could be detected.

Recsk (Heves). The ore and non-ore minerals of the ore masses bound to biotite and amphibolandesites of the Eocene period of the Mátra Mountains: enargite, famatinite, pyrite, tetrahedrite, seligmannite, lautite, galena, sphalerite, bournonite, bornite, boulangerite, emplektite, galenobismuthite, wittichenite, gold, hematite, magnetite, quartz, calcite, dolomite, barite, whewellite.

Secondarily: melnikovite, markasite, redruthite, melanterite, brochantite, pisanite, halotrichite, sulphur, laumontite.

The combination of the elements: S Cu Fe As Sb Pb Zn Ag Bi O Au Si Ca C H Ba Al Mg Se Te.

Parád (Heves). The minerals of smaller ore formations bound to the biotite-amphibolandesite of the Mátra Mountains: quartz, sphalerite, tetrahedrite, galena, pyrite.

Gyöngyösoroszi (Heves). In the strongly alterated lodes of the Mátra bound to unbalanced andesite species containing a lot of quartz varieties. quartz, amethyste, chalcedony, jasper, calcite, pyrite I, galena I, gold, chalcopyrite, sphalerite, wurtzite, stannite, bournonite, galena II, sphalerite II, chalcopyrite, marcasite, pyrite II, jamesonite, semseyite, arsenopyrite, tetrahedrite, antimonite, fluorite, barite, coelestite, gypsum I.

Secondarily: chalcosine, covellite, cerussite, sulphur, laumontite, gypsum II, halloysite.

The minerals of the amygdaloid cavities: apatite, pyrite, sphalerite, fluorite, pennine, chalcedony, rock crystal, opal, calcite, the tuffaceous agglomerates contain apart from these also adularia.

The combination of the elements: O Si Ca S C Zn Fe Pb Mn Mg Cu F H Cd Sb As Ba Sr Al P K Ag Au.

Spectroscopically: Sn Mo can be detected.

Asztagkő (Heves). On the hydrotermal action of the residual solution of the above andesite magma: quartz, barite, antimonite.

Kéked (Borsod-Abaúj-Zemplén). In the pyroxenandesite of the Tokaj-Mountains extending in narrow veins: quartz, chalcedony, marcasite.

Telkibánya (Borsod-Abaúj-Zemplén.) In the trachyte of the Tokaj-Mountains and on the boundary surfaces of trachyte andesite extending in lodes: quartz, opal, pyrite, antimonite, gold, siderite.

Secondarily: alunite, antimony-ocher.

Erdőbénye (Borsod-Abaúj-Zemplén). Extending in veins of andesite of the Tokaj-Mountains: quartz, opal, antimonite.

7. *Not yielding ore, partly laterally secretive hydrotermal.*

The minerals of the cavities of the amygdaloidal basalt surrounding Lake Balaton.

Haláp (Veszprém): phillipsite, desmine, gismondite, natrolite, thaumasite, calcite.

Gulács (Veszprém): magnetite, phillipsite, desmine, chabasite, mesolite, scolecite, natrolite, aragonite, calcite.

Zalaszántó (Veszprém): phillipsite, natrolite, aragonite.

Diszel (Veszprém): phillipsite, chabasite, apophyllite, heulandite, thaumasite.

Sarvaly (Veszprém): phillipsite, apophyllite, heulandite, thaumasite.

Vindornyaszöllős (Veszprém): apatite, phillipsite, apophyllite, natrolite, desmine, calcite.

Zsid (Veszprém): phillipsite, natrolite, calcite.

Badacsonytomaj (Veszprém): phillipsite, aragonite.

Tátika (Veszprém): phillipsite, calcite.

Szigliget (Veszprém): phillipsite.

Kistolmács (Zala): chabasite, desmine, calcite.

The combination of the elements of the mineral association overgrown on the cavities of the amygdaloidal basalt surrounding Lake Balaton: O Si Al Ca C Na K Mg Fe Ba Mn S Cl Sr.

A characteristic feature of the mineral associations contained in the cavities of these slightly alkaline basalt rocks in the permanent occurrence of phillipsite, and in some places that of apophyllite. K is always present in the element association.

The minerals of the cavities of the basalt district of North-Nográd.

Somoskő (Nógrád): in the basalt of Eresztvény mine: phillipsite, aragonite, calcite.

Vecseklő (Nógrád): aragonite.

In the Miocene andesite of the Dunazug Mountains.

Dunabogdány (Pest): pyrite, calcite I, chabasite, desmine, analcime, calcite II.

Visegrád (Pest): calcite.

Szentendre (Pest): pyrite, chabasite.

Szob (Pest): in andesite of the Mt. Csák: chabasite, desmine, epidesmine, calcite.

In the andesite of the Miocene period of Karancs.

In the vicinity of Somoskőújfalu (Nógrád) in the quarry of Sátoros: calcite I, epistilbite, laumontite, heulandite, chabasite, desmine, aragonite, calcite II, dolomite, pyrite, quartz, calcite III;

In the pyroxenandesite of the Mátra (Miocene).

Szücsi (Heves): aragonite.

In the pyroxenandesite of Tokaj-Hegyalja (Miocene).

Füzérkomlós (Borsód-Abaúj-Zemplén): chalcedony, calcite.

Mt. Nagy (Tokaj Mountains): tridymite.

In the rhyolite and andesite of Tokaj-Hegyalja.

Monok (Borsod-Abaúj-Zemplén): chalcedony, milk opal, precious opal.

Tolcsva (Borsod-Abaúj-Zemplén): quartz, jasper, chalcedony, opal.

Megyaszó (Borsod-Abaúj-Zemplén): wood opal.

8. Volcanic exhalation.

Pusztakisfalu (Baranya): in the crinoid limestone of the upper Dogger resulting from submarine exhalation: quartz, hematite, goethite.

Bernecebaráti (formerly Bernece, Pest): in the clay formed by decomposition of the hyperstene-augiteandesite of the Mt. Huszár: tabular scaly hematite.

II. OCCURRENCES CAUSED BY WEATHERING AND SEDIMENTATION

a) Weathering remnants.

Hunting box of Kozár (Mt. Mecsek, Baranya): azurite contained in the breccia filling the fissures of the Triassic limestone.

Tornaszentandrás (Borsód-Abaúj-Zemplén): brown iron ore contained in the limestone (ladinaceous) of the Mt. Osztramos.

(The minerals of the zones of oxidation and secondary enrichment of the occurrences of magmatic origin are discussed in the part dealing with the mineral association of the respective mining district).

b) Mechanical sedimentations.

In fluviatile placers of the Duna (Ásvány, Ráró, Hédervár) Dráva and Mura: gold.

Visegrád, Szokolya (Pest), Drégelypalánk: garnet (almandine).

Tatabánya (Bánhida, Komárom): in sandy clay saphire, zircon, garnet.

Siófok (Somogy): in the sand of the Balaton zircon and ilmenite.

c) Chemical sedimentations.

1. Ores.

Manganese oxide ores formed partly from sea sediments in the interstices of the Jurassic sediments, mainly in the marl clay of the upper Liassic, but also partly through the oxidation of the carbonateous sediments.

Urkut (Veszprém): pyrolusite, cryptomelane, psilomelane, magnetite, limonite, marcasite, quartz, calcite.

The combination of the elements: O Mn Fe Si Al K Ca H Ba Na Mg P C.

Spectroscopically Sr and Rb can be detected.

Eplény (Veszprém): pyrolusite, manganite, cryptomelane, psilomelane, limonite, quartz, (chalcedony, jasper, rock crystal) calcite.

The combination of the elements: O Si Mn Fe Al K Ca H•Ba Na Mg P C.

Spectroscopically Sr and Rb can be detected.

Lábatlan (Komárom): in the limestone of the meso Liassic in the quarry of the Tölgyhát of the Gerecse Mountains: pyrolusite, manganite, psilomelane, chalcopyrite, barite.

Almagyar (Heves): in Oligocene clay: pyrolusite.

Bátor (Heves): in Oligocene clay: pyrolusite, manganite.

Cserszegtomaj (Veszprém): bog iron sulphide separated in the upper-Pannonian layer of the Keszthely-Mountains: melnikovite, marcasite.

Balf (Sopron), Nemesvite (Zala), Lesencfalu (Zemplén): gnarly and crystallized marcasite in clay.

Mád (Borsod-Abaúj-Zemplén): the ores of Dióshegy formed from spring sedimentation: limonite containing a small amount of pyrolusite, ungvarite.

Nagyléta, Bagamér (Hajdú): vivanite and bog iron ore.

2. Evaporites.

Perkupa, Tornakápolna (Borsod-Abaúj-Zemplén): in the Werfen layers: anhydrite, gypsum, halite, glauberite.

3. The mineral occurences of the Hungarian bauxite mines.

Iszkaszentgyörgy, Gánt (Fejér), Nyirád (Veszprém): alunite. In Gánt pyrite and in the clay gypsum.

4. Other minerals.

Aggtelek, Lillafüred (Borsod-Abaúj-Zemplén): stalactite contained in the limestone of the Triassic period.

Csővár (Pest): fluorite contained in limestone of the Triassic period.

Szentgál (Veszprém): calcite in »Dachstein« limestone.

Üröm (Pest): aragonite in »Dachstein« limestone.

Lábatlan (Komárom): aragonite in limestone of the Liassic period. (Nagypisznice).

Buda (Pest): hornstone gnarls in dolomite of the Triassic, sometimes containing quartz. In nummulinous limestone of the Eocene period: calcite, barite, fluorite, pyrite, limonite, goethite.

In clay of Kiscell of the Oligocene period: limonite pseudomorph after pyrite and marcasite, barite, calcite, gypsum.

In limestone tuffs: pisolite.

In nummulinous limestone of the Eocene period:

Békásmegyer (Pest): calcite

Kosd (Pest): calcite, marcasite, gypsum

Tokod (Komárom): calcite

Dorog (Komárom): calcite, aragonite

Halimba (Veszprém): pyrite, limonite

Tatabánya, Felsőgalla (Komárom): aragonite

Sümeg (Veszprém): calcite.

In limestone of Lajta:

Kemence (Pest): calcite

Hidas (Baranya): calcite

Márkháza (Nógrád): calcite

Of the numerous calcite occurrences of Hungary only those are enumerated which have already been crystallographically elaborated.

Komlóska (Borsod-Abaúj-Zemplén): spring limestone, manganese ore in traces.

Székesfehérvár (Fejér): pinquite.

Gönc (Borsod-Abauj-Zemplén): ungvarite.

In the Hungarian brown-coal mines:

Ajka (Komárom): marcasite,

Tatabánya (Komárom): alumino-hydrocalcite, pyrite, calcite.

Dorog (Komárom): huntite.

Tokod (Komárom): halotrichite, tschermigite.

d) Minerals of organic origin.

Zengővárkony (Baranya): between alterated trachydolerite and granular Dogger limonite of biogene origin, some goethite.

Buda (Pest): in clay of Kiscell: kiscellite, and a krantzitelike resin.

Ajka (Veszprém): ajkaite contained in brown-coal of the upper Cretaceous period and on the waste tips sulphur.

Pilisszentiván (Pest): on the waste tip of the brown coal mine originating in the Paleocene period: sulphur.

Serényifalva (Borsod-Abaúj-Zemplén): resin contained in clay of the Oligocene period belonging ot the rumenite-krantzite group.

III. Metamorphic mineral associations.

Minerals from the crystalline bottom mountain ranges of Kőszeg:
Velem (Vas): fuchsite, manganese in traces.
Felsőcsatár (Vas): talc, serpentine.
Csák (Vas): quartz, pyrite.

IV. Meteorits found in Hungary:

Siderite: Nagyvázsony (Veszprém) 1890.
Aerolites: Kaba (Hajdu) 1857, Ófehértó (Szabolcs) 1900, Malomháza (Sopron) 1905, Kisvarsány (Szabolcs) 1914, Mike (Somogy) 1944.

REFERENCES:

1. Leonard C.: Handbuch einer allgemeinen topographischen Mineralogie. 1805—1809.
2. Schönbauer V.: Minerae metallorum Hungariae et Transsylvaniae. 1809—1810. Viennae.
3. Zipser A.: Versuch eines topographisch-mineralogischen Handbuches von Ungarn. Oedenburg. 1817.
4. Zepharovich V.: Mineralogisches Lexicon für das Kaiserthum Österreich. I. 1859, II. 1873., III. 1893. Wien.
5. Cotta—Fellenberg: Die Erzlagerstätten Ungarns und Siebenbürgens. 1862, Freiburg.
6. Tóth Mike: Magyarország ásványai. 1882. Budapest.
7. Koch Sándor: Magyarország jelentősebb ásványelőfordulásai. 1931. Budapest.
8. Vadász Elemér: Magyarország földtana. 1953. Budapest.

THE QUALITATIVE DETERMINATION OF CLAY MINERAL GROUPS BASED ON COLOUR REACTION[1]

BY J. MEZŐSI

PRELIMINARY REPORT

INTRODUCTION, METHODS OF INVESTIGATION.

For the solution of many scientific and practical problems the exact knowledge of the mineral composition of clays is important. A common characteristic of clay minerals is that they mostly crystallise very difficultly, consequently, they usually occur as minute crystals (the diameter of their granule not exceeding 0.0002 mm in size).

Considering the importance of clay minerals, various methods were elaborated for their determination.

The more important ones are as follows:

1. *Optical method.* This method can only be used if the size of the granule components does not exceed the clayey fraction, i. e. they are at least 2 microns in size or larger. Kaoline is almost the only clay mineral which corresponds to this postulate. The bulk of the other clay minerals are about the size of colloids or still small. Hence the smallness of the grain sets a limite to the use uf optical determination methods. Considering that the qualitative determination is already difficult the quantitative one is still more complicated. Apart from this the changes in the external conditions renders the application of the optical method still more intricate. Thus, for instance, at the determination of the value of the refraction index and of the magnitude of the double refraction such factors as temperature, pressure, the quality of the embedding liquid, wave length, etc. all play a role. Concerning the effect ot the environment it should only be mentioned that, e. g. montmorillonites can take up water various cations etc. between their interlaminar layers which influence the refraction of light to a great extent. [3, 18, 19, 20]

2. *The electronmicroscopic and röntgenographic methods* of determination yield exact results, however, owing to the intricate and expensive equipment needed, their application is no easy matter so that these methods cannot be generally used.[12, 14]

3. A disadvantage of *the chemical methods* is that the analyses do not always furnish suitable results. In this respect the fact, that whithin

[1] Delivered as a lecture to the Geochemical Commission of the Hungarian Academy of Science at its Meeting in April 1954.

the same kind of mineral the chemical composition varies very much, that certain ions can substitute one another to a great extent, as well as the base exhange capacity, the variations of the water content, the great adsorbtion ability, etc.[4, 14] must all be taken into account.

4. The examinations carried out by means of *differential thermal analyses* supplement the X-ray examinations. The disadvantage of this method is that its exactness depends upon many factors: fineness of the pulverization, the impurities, etc. Thus the data reported by the different authors cannot be compared at first hand, whereas in the case of the results obtained with X-ray examinations this is possible. Hence by differential thermal investigations for each apparatus a comparison curve must be previously prepared from the pure substance. This method was elaborated in Hungary by Mrs. A. Földvári. With her method quantitative determinations within an error range of 0.5 per cent can also be performed.

5. It is known that the interlaminar adsorbtion of the montmorillonoid group which can be brought about by an excess charge can alter the interlaminar distance in a characteristic manner. As organic molecules can also be built in organic complexes may form, too. On this basis already some time ago *colour methods* were elaborated for the montmorillonoid groups. Initially aniline and aso dyes, later amines were used for the investigations.[1, 2, 5, 9, 10, 11, 13, 15, 16] Other workers carried out experiments with benzidin.[16, 21] The mechanismus involved at the colouration of the clay surfaces,[21] as well as the relation between the ionic substitution of montmorillonits and swelling were examined.[2, 21] The different types of colour tests were in the first place used for the determination of the montmorillonoid group.

Of the investigations reported particularly the results published by Hauser and Leggett[10] are valuable. In their work all the organic subtances involved at the coluration of clays are listed in tables. The experiments were carried out with Wyoming bentonite, hence their results are only valid for montmorillonoid groups. As they established that certain compounds do not exhibit colour reactions (certain anilines, aliphatic amines, saturated cyclic amines, nitrobenzene, heterocyclic nitrogen compounds, furthermore organic compounds where there are no amine groups on the benzene ring did not show colour reactions; the acetyl group, bound to the nitrogen, NO_2, SO_3, H, acetyl, Br, OH inhibited the colour reaction, the methoxyl and ethoxyl groups lightened the colour) the investigations were, of course, continued with those groups of compounds where colour formation could be observed.

The colouration produced by the organic compounds examined by Hauser and Leggett could not always by precisely identified. The authors obtained with orthotoluidine on bentonites in alkaline medium a yellow and in acid medium a pink colouration. Bosazza[1] and the author, however, observed in alkaline medium a green, in a neutral one a bluish green and in acid medium an orange yellow colouration.

Hambleton and Dodd[9] carried out their experiments with para-aminophenol with which compound Hauser and Leggett could not detect a colour reaction. This procedure is, however, very

uncertain, as for instance when HCl was added dropwise into the alcoholic solution of para-aminophenol — according to the prescription published by the former two authors — and then left to dry, a bluish lavendel colour appeared which according to them is characteristic for the montmorillonoid group. It is, however, also probably that the purity of the compound influences to a great extent the colour production and unfortunately no chemically pure para-aminophenol was available to the author of this paper.

EXPERIMENTAL RESULTS.

The respective compounds were also examined as to what colour they show in alkaline or acid medium and as to whether the produced colour does not interfere with the colouration of the complex compounds formed on the clay samples. If the compound exhibited in acid or alkaline medium without the addition of any other substance a colour reaction it was not further examined as the colour would as it is have caused an interference.

Concerning the concentration of the solutions — but for the one para-aminophenolic examination — the author could not find any reference in the literature. Thus to obtain the most suitable colour intensity solutions of 10, 1 and 0.1 per cent were prepared. In the case of caoline, when benzidine was used, no essential difference could be found between the solutions of 1 and 0.1 per cent. On increasing the concentration the undissolved (?) benzidine on the surface of the suspension interfered. With montmorillonite when a solution of 10 per cent was used the result was the same as with caoline, a solution of 1 per cent yielded a fine Berlin-blue colour, one of 0.1 per cent a somewhat less distinct colour. With illite a solution of 10 per cent furnished a pale blue colouration, on using a solution of 1 and 0.1 per cent the colour became still lighter.

Of orthotoluidine also solutions of 10, 1 and 0.1 per cent were prepared. In the case of the caoline group if a solution of 10 per cent was used the surface resembled that observed with benzidine. With a solution of 1 per cent a turquoise green colour appeared, with a solution of 0.1 per cent the colour faded somewhat. In the case of mortmorillonite with a solution of 10 per cent like in the latter case no proper colouration could be detected, whilst on using a solution of 1 per cent the colour of the suspension became greenish blue, with one of 0.1 per cent a lighter colour was produced. With the illite group the colour resembled that of caoline when solutions of varying concentration were used.

Solutions of 10 and 0.1 per cent were prepared from diphenyl amine. However, in this case, considering that the reaction runs down more rapidly in a hydrochloric acid medium, the addition of different concentrations of HCl was also attempted. For all three mineral groups the diphenyl amine concentration proved to be the most suitable, if a solution of 1 per cent was used, whereas the variation of the hydrochloric acid concentration did not influence essentially the course of the reaction. For all further experiments HCl was used in a solution of 10 per cent.

The series of experiments revealed that for these compounds a solution of 1 per cent proved to be the most suitable concentration.

Earlier authors who have dealt with this problem were of the opinion that only certain factions of the substance are suitable for the determination. They examined the resulting colouration on single granules under the microscope. The author of the present paper, on the other hand, pulverised in all his experiments the substance to be examined in a mortar. In every case a solution of 1 per cent was prepared from the respective organic compounds and a suspension of the substance to be examined was made with this solution in small white coloured porcelaine dishes. In this manner the colour reaction could be easily observed with the naked eye. As far as possible the compounds used for the experiments were always pure chemically.

The composition of all substances used for the experiments, as well as their structure are all known on the basis of previous investigations, they represent characteristic samples of the different clay mineral groups. The samples occurred at the following deposites: the caoline at Zettlitz, the montmorillonite at Gönc and the illite at Füzérradvány. The samples were furnished by Mrs. Földvári the head of a department of the Geological Institute and the author wishes to express his sincere gratitude to her for her kindness. The author is also very much obliged to the Hungarian Mining Research Institute for providing the substances needed for the experiments, they were made available from the following places. Gönc, Mád, Komlóska, Istenmezeje and Nagytétény.

With various organic compounds the following results were obtained:

BENZIDINE (4 4' diamino-diphenyl).

Weil, Malherbe and Weiss[21] consider the blue reaction of benzidine to be an oxidation-reduction mechanism.

Some authors are doubtful as to the utility of benzidine, amongst others only a paper published by Page[15] should be mentioned. On the other hand, the investigations of Siegl[16] and other authors proved that it is suitable for the determination of montmorillonite, particularly in a neutral medium. Hauser and Leggett,[10] mainly on the basis of the investigations of Stern, also find it appropriate for the determination of the montmorillonites. On using it for the minerals of the caoline group Bosazza[1] did not obtain a colour reaction either in a wet or in a dry state, with montmorillonite and illite (!) on the other hand, he observed a Berlin-blue colouration. He mentions that the caoline which he examined, though it contained a considerable amount of ferrous and ferric iron, did not show any colour reaction. With the exception of Bosazza[1] all investigators did not take the pH values into consideration.

The author of this paper the colours produced during the reaction by the means of the UNESMA[22] colour scale.

Our investigations have proved that benzidine is suitable for the determination of montmorillonoide groups through the colour reaction the latter can be well distinguished from the caoline- and illite groups. After standing for a fairly long time the reaction also runs down if a dry solid reagent is added to the clay sample. The deepness of the blue

sample deposite	p_H 1—2		p_H 6 7		p_H 9—10	
	wet	dry	wet	dry	wet	dry
caoline Zettlitz	no changes	white light yellow (11 ga) border	light blue (17 ca)	light blue (17 ga) fading gradually finally white	no changes	no changes
montmoril-lonite Gönc	green (24 1a)	darker green (24 pg)	Berlin blue (15 pa)	dark blue (15 pi) changing gradually green, yellow, finally white	light ochre yellow (2 pc)	light brown (3 lg)
illite Füzér-radvány	no changes	no changes	light blue (16 ca)	light blue (17 ga) fading gradually finally white	no changes	no changes

colouration shows to a certain extent how much of the montmorillonoide group is contained in the respective clay. In such cases the characteristic Berlin-blue colouration is somewhat diluted. The mixture of mineral groups contain every transition colour from the light blue of caoline or illite to the characteristic Berlin-blue of montmorillonite. A disadvantage of using benzidine for the investigations is that the caoline and illite groups cannot be differentiated from each other.

In the course of drying the colour gradually changed from blue to green and yellow, becoming finally colourless. If water was added to the substance after it had been dried it soon took up its original colour. Weil, Malherbe and Weiss[21] only obtained a weak colour reaction with montmorillonite and caoline, the intensity of the colour also only increasing slowly, whereas at the experiments of the author of this paper the colour reaction took place rapidly under the conditions described above.

ORTHO-TOLUIDINE (ortho-aminotoluene).

Hauser and Leggett[10] also carried out experiments with the homologues of aniline ortho-, meta- and para-toluidine. They obtained with ortho- and meta-toluidine in the case of bentonite in alkaline medium a yellow colour and in acid medium an orange one, whereas with para-toluidine a pink colouration only in proportion to the amounts appeared in alkaline medium.

sample deposite	p_H 1–2		p_H 6–7		p_H 9–10	
	wet	dry	wet	dry	wet	dry
caoline Zettlitz	no changes	light yellow (10 ca)	light green (20 ca)	the green (20 ga) colour fading gradually (20 ca)	no changes	no changes
montmoril-lonite Gönc	yellow (2 na)	crange becoming gradually darker (3 pa 4 pa)	bluish green (18 pa)	bluish green (18 pa) turning after being kept for a fairly long time orange (3 pa)	dark green (24 ng)	brown (3 pi)
illite Füzérrad-vány	no changes	light yellow (l ca)	light green (20 ca)	light green (20 ca)	no changes	no changes

The author of the present paper only carried out experiments with ortho-toluidine, the result are summarised in the following table.

The table shows that ortho-toluidine is very suitable, particulary in a neutral medium, for the determination of montmorillonite. It also yields the corresponding values in alkaline and acid medium, but only for montmorillonite. The differentiation of the caoline and illite group is also difficult in this case. If montmorillonite is mixed with illite or caoline the characteristic green colour is diluted and in proportion to the amount of the mineral groups all colours from a light greenish blue to the dark greenish blue of pure montmorillonite can be produced.

Bosazza[1] also accomplished experiments with ortho-toluidine. It is interesting that he did not obtain any colour reaction with any of the minerals of the caoline group. With bentonite and montmorillonite he did not either achieve any results. In the course of the examinations of the author illite showed only a weak colour reaction, whilst Bosazza[1] could only detect a dirty green colouration in the case of this mineral group.

The author let ortho-toluidine undergo reactions with ferrous and ferric compounds. In the case of ferrous compounds there was no change of colour, in that of ferric ones the solution showed a green colour. Thus ferric ions certainly play a significant part in the production of colour reactions.

DIPHENYLAMINE

Hauser and Leggett[10] obtained with montmorillonite both in acid and alkaline mediums a blue colouration, however, they do not describe the experimental conditions. Bosazza on the other hand, only succeeded in observing a dirty green colouration with activated Fullers earth, whereas in the case of caoline-, montmorillonite- and illite groups in moistened and dry no colouration could be observed.

The results of the experiments of the author are illustrated in the following table:

sample deposite	p_H 1—2		p_H 6—7		p_H 9—10	
	wet	dry	wet	dry	wet	dry
caoline Zettlitz	light green (23 ga)	green (24 le) fading gradually	no change	white with a light bluish border (17 ca) light blue (16 ga)	no change	no change
montmorillonite Gönc	green (21 na)	green (23 pi) fading gradually	green (23 nc)	green (23 nc) becoming gradually darker (23 pi)	no change	no change
illite Füzérradvány	grass green (23 na)	light green (22 ca)	no change	white becoming gradually light blue (16 ga)	no change	no change

With an alcoholic solution of 1 per cent of diphenylamine a suspension was prepared in a neutral medium the reaction taking place very slowly, the colouration only appeared after the substance had dried. In acid medium the reaction ran down relatively quickly, about within an hour. The experiments show that particularly in acid medium the montmorillonite group can be well distinguished from the caoline- and illite ones, respectively. However, this procedure has also the disadvantage that the caoline and illite groups cannot be differentiated from each other, furthermore that in the case of a caoline-montmorillonite mixture neither the lighter green colour of caoline, nor the darker green one of montmorillonite can be distinctly detected, but that in proportion to the mixture transition colours appear.

DIMETHYLANILINE.

It belongs to the tertiaery amines.

This organic compound was only examined by Hauser and Leggett[10] on Wyoming bentonite. The author of the present paper did not only examine caoline and illite but also extended his experiments to montmorillonite. When the pulverised substance was mixed with the reagent the substance of all three mineral groups turned light green resembling the colour of dimethylaniline. The colours could only be distinguished, in the course of the drying of the substance caoline turning brownish green, montmorillonite dark green and illite light green. When the substance was dryed the colours changed, caoline showed a light green colouration, montmorillonite no change of colour and illite became colourless. After being kept for some time, first caoline and illite, later also montmorillonite exhibited a blue and eventually a pink colour already previously observed.

*

The disadvantage of the examination methods used so far is that they are only suitable for proving the presence of montmorillonite and for the distinction of montmorillonite from caoline and illite groups. However, they do not render possible the establishment whether caoline or an illite group, or a mixture of these clay mineral groups is involved. For this purpose the author performed experiments with several groups of organic compounds, among others with phenols. The latter have — as is known — an acid character and combine with alkalies to form salts. The acid character becomes more pronounced if not only a hydroxil radical, but a nitro radical is also substituted. The following compounds proved to be suitable: para-dioxybenzene (also called hydrochinone), used for photography, para-methylaminophenol (methol) and para-methylaminophenol-sulphate. A solution of 1 per cent was also prepared from these compounds for the experiments. Experiments with pure substances yielded the following results at pH 6—7.

On using a solution of 1 per cent of paramethylaminophenol and paramethylaminophenolsulphate montmorillonite turned immediately light green. This colour gradually faded. With para-dioxybenzene at first no change could be observed in either group, later after standing for a fairly long time the green colour of montmorillonite faded completely and the colour of the substance to be examined showed at the most a light greenish tint. At the same time caoline also began to undergo a change, with para-methylaminophenol and para-methylaminophenol sulphate a greenish brown, with para-dioxybenzene a pink colouration could be observed. This reaction ran down relatively slowly lasting about one day. In alkaline medium on the action of any of the three reagents the liquid above the substance turned brown. This could be seen in the case of all three samples. Caoline and illite remained colourless, whereas the whole of the montmorillonite took up a greenish brown colour (2pc). In acid medium the light green colour of montmorillonite disappeared at once, gradually, however, it after all changed again to a green colour

reagent		caoline	montmorillonite	illite
para-dioxy-benzene (hydrochinone)	wet	gradually pinkish brown (6 pg)	no change	no change
	dry	reddish brown	no change	no change
para-methyl-aminophenol (methol)	wet	gradually brown (2 ng) greenish	light green (24 ic) fading gradually	no change
	dry	brownish green (l pu)	colourless	no change
para-methyl-aminophenol-sulphate	wet	gradually greenish brown (2 ng)	light green (24 ic) fading gradually	no change
	dry	brownish greenish (l pn)	colourless	no change

later displaying a bluish tint (19ne). Caoline and illite, on the other hand, do not change either in a wet or a dry state and do not show any colour reaction. If pure caoline and illite were mixed in a ratio of 1 : 1, the suspension prepared from a solution of 1 per cent of para-methylamino-phenol sulphate was at first — as long as it was wet — colourless eventually it turned greenish brown which colour also persisted when it was dry. A mixture of caoline and montmorillonite 1 : 1 behaved in the same way. A mixture of montmorillonite and illite 1 : 1 did not show any change whether it was wet or dry. Control experiments were carried out with bentonite from Istenmezeje it was pulverised and a suspension prepared not either showing any colour reaction. According to the data reported in the literature bentonite from Istenmezeje consists of 85 per cent montmorillonite and 12 per cent illite. The fact that the clay minerals are not pure could already be established in the course of the examinations with benzidine, inasmuch as a deep Berlin blue colour could not be observed. This method makes it obvious that only the caoline group undergoes an essential change, hence it is easy to distinguishe it from montmorillonite and illite. These two latter groups, on the other hand, can be readily differentiated with any of the methods using amines.

An experimental series was devised to keep the different clay mineral types at various temperatures for an hour in order to observe at

which temperatures they undergo a colour reaction. As the action of benzidine is very rapid and intensive a suspension of a benzidine solution of 1 per cent was prepared from samples heated to different temperatures, of course, the heated sample was first cooled to room temperature.

The following results were obtained:

temperature C°	caoline		montmorillonite		illite	
	wet	dry	wet	dry	wet	dry
110	characteristic colour reactions					
200						
500	greenish grey not characteristic	no changes	15 pa (green)	15 pa	characteristic colour reaction	
600	no changes	no changes	green (15 pa)	15 pa		
700	no changes	no changes				
800	—	—	no changes	no changes	—	—
900	no changes	no changes	no changes	no changes	no changes	no changes

The experiments proved that relatively the caoline group is the most sensitive to changes of temperature, a sample heated to 500° C and subsequently cooled did not any more show a characteristic colour reaction. If we compare this with the values obtained by means of differential thermal analysis reported in the literature[7, 8, 12] it can be established that in the case of most caolines at a temperature of 500—550° C an endotherm change results depending upon which of the members of the caoline

group are present. The separation of the hydroxyl radicals results in the decomposition of the crystal lattice. Hence it is obvious that such samples do not exhibit a colour reaction.

In the case of montmorillonite a bentonite sample from Istenmezeje first heated to 500° C and 600° C and then cooled, showed instead of the characteristic Berlin-blue colouration a dark green one (15 pa). Another sample heated to 700° C exhibited the same colour, the only difference being that when benzidine was used for the suspension of the pulverised sample ist colour was of a lighter tint. Both wet and dry suspensions prepared from a sample heated to 800° C and still higher temperatures no longer showed any colouration. The curves plotted on the basis of the differential thermal analyses reported in the literature show that the decomposition of the crystal lattice and the separation of the OH radical of the various members of the montmorillonoide family occurs at different temperatures: with nontronite at 450—500° C, with montmorillonite at 600—700° C and with hectorite at 700—900° C. It may therefore be assumed that probably it is possible to determine the mineral species within a montmorillonoide group more exactly. In this respect bentonite from Istenmezeje was examined, the presence of montmorillonite could undoubtedly be established in it, however, it stands to question what cause the appearence of the dark green colour instead of the blue one of benzidine.

Although the OH radical of the illite group separates at a temperature range of 200—600° C the crystal lattice persists, at the most the lattice constants increase to a small extent. The structure disintegrates gradually the complete decomposition only taking place at 800—900° C. On heating, the illite showed a light greenish blue colour reaction till the temperature reached 700° C above it both wet and dry suspensions prepared from this substance did not undergo any further change. After standing for some time the green colour turned gradually greenish blue.

The experiments point to the fact that within all three mineral groups a colour reaction only takes place as long as the structure is intact, if the structure disintegrates a colour reaction does not take place any more. It will be attempted to extend the method of examination not only to render possible a quick and certain determination of pure substances, but also of mixtures. We shell try to establish which compounds are more reactive those of acid or those of alkaline character, furthermore to what extent the colour reaction is sensitive to the changes of the pH and finally to examine the substance yielding a colour reaction under the microscope. It would also be useful to extend the investigations to the determination of soils. However, in this case it must be taken into account that their darker colour will cause difficulties.

Later it will be possible to control and supplement the results through comparing them with the values obtained with the differential thermal analyses. It seems also desirable to examine the complex compounds forming at the colour reactions more closely.

An advantage of the method is that the different clay mineral groups can be readily determined in the areas of occurrence rendering the investigation of these kinds of crude substances far easier. Another important field of research is oil mining where the quick determination of the clay

mineral groups is also a significant factor. If the method can be improved it may under certain conditions also be suitable for the identification of the geological strata.

REFERENCES:

1. Bosazza V. L.: On the adsorbtion of some organic dyes by clays and clay minerals. Amer. Mineral. 29. 1944. 235—241.
2. Buzágh Aladár: Bentonit szolok és bentonit gélek sajátságairól. Magyar Kémiai folyóirat. 56. 1950. 7—10.
3. Correns C. W.: Bestimmung der Brechungsexponenten in Gemengen feinkörniger Minerale und von Kolloiden. Fortschritte der Min. Krist. und Petr. 14. 1929. 26—27.
4. Engelhardt W: Über silikatische Tonminerale. Fortschritte der Min. Krist. und Petr. 1937. 21. 276—340.
5. Faust G. T.: Staining of clay minerals as a rapid method of identification in natural and beneficiated products. U. S. Bureau Mines R. I. 3522, 21, (1940).
6. Foster Margaret: Geochemical studies of clay minerals.. II. Reaction between ionic substitution and swelling in montmorillonites. Amer. Mineral. 33. 1953. 994—1006.
7. Földváriné, Vogl Mária: Agyagásványok differenciális termikus vizsgálata. Földtani Közlöny. 1951. 91—96.
8. Földváriné, Vogl Mária: Magyar bauxitfajták ásványos összetételének vizsgálata differencialtermikus elemzéssel. M. T. A. Műszaki Tudományok Osztályának Közleményei. V. 3. 1952.
9. Hambleton W. W. and Dodd, Ch. G.: A qualitative color test for rapid identification of the clay mineral groups. Economic Geol. 48. 1953. 139—146.
10. Hauser E. A. and Leggett M. B.: Color reactions between clays and amines. Jour. Amer. Chem. Soc. 62. 1940. 1811—1814.
11. Hendricks S. B. and Alexander L. T.: A qualitative color test for the montmorillonite type of clay minerals. Jour. Amer. Soc. Agronom. 32. 1040. 455—458.
12. Jasmund K.: Die silicatischen Tonminerale. Monographien zu „Angewandte Chemie" and „Chemie Ingenieur-Technik". Weinheim, 1951.
13. Marshall C. E: Mineralogical Methods for the Study of Silts and Clays. Zeitschrift für Kristallographie, 90, 1935. 8—34.
14. Nemecz Ernő: Az agyagásványok kristályszerkezete és röntgenvizsgálata. Földtani Közlöny 1953. 182—196.
15. Page J. B.: Unreliability of the bensidin colour reaction as a test for montmorillonite type of clay minerals. Soil Science, 51. 1941. 133—140.
16. Siegl W.: Über den Nachweis von Montmorillonit mit Benzidin. Neues Jahrbuch für Mineralogie, Geol. und Paleont. Monatshefte. 1945—48. Abt. A. 40—42.
17. Tittel Oszkár: A bentonit, mint öntödei segédanyag. Bányászati és Kohászati Lapok 1949. 490—495.
18. Vendel Miklós: Ein Verfahren zur Bestimmung der Lichtbrechung silicatischer Tonminerale vom Montmorillonit—Nontronittyp. M. Kir. József Nádor Műszaki és Gazdaságtudományi Egyetem Bánya és Kohómérnöki osztályának közleményei. Sopron. 1943. 330—343.
19. Vendel Miklós: Zur Bestimmung der Lichtbrechung silicatischer Tonminerale. Chemie der Erde, 15. 1945. 325—370.
20. Vendel Miklós: Szilikátos agyagásványok meghatározása. Bányászati Lapok 1951. 14—17.
21. Weil H., Malherbe and Weiss J.: Colour reactions and absorbtions of some aluminosilicate. J. Chem. Soc. 1948.
22. Unesma: 24 Farbentafeln. Leipzig, 1933.

ELECTROCHEMICAL EXAMINATION OF THE OXIDATION PROCESSES OF SULPHIDE ORES

FROM THE ELECTROMOTIVE FORCE SERIES OF SULPHIDE ORES:

BY GY. GRASSELLY

INTRODUCTION, THE SO FAR OBTAINED RESULTS:

The hitherto performed examinations concerning the weathering of sulphide ores have shown[1, 2] that the essence of the problem cannot be approached if the weathering of the sulphide ores is considered to be a purely chemical process, a simple chemical solution. All observed facts cannot be attributed to simple chemical changes (e. g. the change of the free sulphur content of the solutions circulating over various ore fragments and that of their total sulphate content, respectively, as well as the change of the pH of the solutions etc.). For instance that at the end of the experimental series the 0.05 N sulphuric acid circulating over a tetrahedrite fragment contained mainly ferrous and only to a small extent ferric iron, whereas under similar conditions in solutions circulating over other ores ferric iron dominates. It is also due to the above mentioned fact that in the solutions circulating over the tetrahedrite sample the separation of iron hydroxide could not be observed, although its free sulphuric acid content was lower and its pH higher than that of solutions circulating over other ores in which, on the other hand, iron hydroxide separated in ample amounts. The investigation of the interaction of systems with different redox potential consisting of metal ions (Cu, Fe, Mn) with different valences also affords a quantitative explanation of the problem as has also been pointed out[2] on the basis of qualitative examinations in the course of simple chemical tests.

In our papers mentioned above relating to the solution and oxidation of sulphide ore, more precisely that of some more important sulphide ores the decisive importance of the influence of the environment was already stressed. This is, of course, no new establishment as it has already been referred to by numerous authors, consequently not only the oxidation and solution of pure, or at least apparently pure ores were investigated, but also ore mixtures which can also actually be found in nature. These investigations, as well as those[3, 4] aiming at the development of the electrochromatographic and the electrolytic structure etching methods pointed to the appropriateness of the electrochemical examination of ores, in the first place to that of their electromotive force series. However,

to be able to furnish not only qualitative data, but also a quantitative interpretation of the processes occurring during weathering on the systems occurring in nature electrochemical detailed investigations must be carried out taking the different active components into consideration.

Gottschalk and *Buehler*[5] performed as far beck as 1910—1912 also experiments concerning the establishment of the electromotive force series of ores who dealt with the oxidation of sulphide ores. They measured the potential of the different ores to metal copper in distilled water. On the basis of their measurings they established the following sequence:

Marcasite	0.37 V	Galena	0.15 V
Argentite	0.23	Chalcocite	0.14
Chalcopyrite	0.18—0.30	Niccolite	0.02
Enargite	0.18—0.23	Domeykite	0.01
Molibdenite	0.20	Metal copper	0.00
Covellite	0.20	Antimonite	− 0,17 — − 0.60
Pyrite	0.18	Sphalerite	− 0.20 — − 0.40
Bournonite	0.17		

Wells[6, 7] performed similar examinations. According to him the potential of the various ores differs essentially if measured in acid or in alkaline medium. *Rosenkränzer*[8] also refers to the significance of the electromotive force series and establishes that the extent of the solution of sphalerites is in proportion to the amount of iron and pyrrhotite they contain, the more they contain the greater the solution.

Recently *Rechenberg*[9] dealt with the electromotive force series of ores. His results will be briefly mentioned here. He accomplished his more precise examinations with a valve-voltmeter the input resistance of which was 10^{12} Ohm reducing the current consumption of the apparatus and the occurring polarization phenomena to a minimum through the suitable construction of his apparatus. On the Multiflex MG 2 galvanometer which he used 1 scale division = 1 mm = 1 mV. The composition of the solution used by him corresponds to the composition of the mine inflow circulating over a certain lead-zinc deposite, containing 100 g NaCl, 22 g $CaCl_2$, 0.022 g $FeCl_2$, 0.74 g $BaCl_2$ per liter and SO_4'' in traces. The pH of the solution was 4. The readings were taken $^1/_2$ minute after the ore had been immersed into the solution. The results of his paper, only taking the data concerning the sulphide ores into consideration, are as follows:

I.		II.	
Pyrite	658 mV	Marcasite	646 mV
Marcasite	634	Pyrite	540
Chalcopyrite	558	Bornite	454
Sphalerite	459	Chalcopyrite	453
Covellite	448	Covellite	434
Bornite	416—448	Chalcocite	416

I.		I.	
Pyrrhotite	398,5	Molibdenite	411
Galena	395	Argentite	358
Argentite	276	Galena	328
Native copper	196	Native copper	199
Antimonite	120,5	Sphalerite	181
Chalcocite	111	Antimonite	96
Molibdenite	109,5	Hydrogen	0,000
Hydrogen	0,000		

The identical ores of the two sequels are of different origin. The sequel is the result of the measuring of the electrode potentials to a calomel electrode which were recalculated by Rechenberg for a normal hydrogen electrode in order to obtain an electromotive force series of ores which is analogous with that of the metals.

SULPHIDE ORES AS POLYELECTRODE SYSTEMS:

A heterogeneous polished ore surface can be considered to be a short-circuited polyelectrodic galvanic cell on the surface of which numerous micro cathodes and micro anodes may occur. To put it more simply: both of the two sulphide ores if they come into contact with a given solution possess a certain electrode potential. Among the two phases of the system the one is more positive than the other. On direct contact, which usually occurs with polished sections and ore lodes in general, should the ohmic resistance be low in order to restore the electric equilibrium the intensity of the current between the two phases can assume relatively high values which in turn corresponds to a significant chemical alteration. In the phase playing the role of the negative pole of the different macro- or micro galvanic cells consisting of two different ores this electrochemical reaction results in the formation of cations i. e. in the solution of the phase. The ore with a more positive potential behaves as cathode, the less positive one as anode. As the extent of the solution of an anode depends among other factors also upon the size of the cathodic surface the smaller the cathode behaving as inclusion or impurity as compared to the anode, the smaller will be the extent of the solution of the anode due to electrochemical causes. The relatively great resistance of very pure ores to solution also supports this assumption.

For instance a 0.05 N sulphuric acid solution circulating over 300 g of selected really pure chalcopyrite fragment contained at the end of the experimental series an amount of copper corresponding to 0.0836 g chalcopyrite per liter, which corresponds to the dissolution of 0.418 g chalcopyrite assuming that 5 liter solution circulated over the fragment; i. e. 0.13 per cent of the pure chalcopyrite dissolved. On the other hand, under entirely similar conditions a solution circulating over 300 g pyrite fragment, containing as mechanical impurity 6,06 per cent chalcopyrite, thus altogether 18.18 gr, contained at the end of the experimental series

an amount of copper corresponding to 0.7969 g chalcopyrite per liter, hence again assuming the circulating solution to be 5 liter, of the chalcopyrite which was in direct contact with the pyrite a total amount of 3.98 g dissolved, i. e. 22.1 per cent of the chalcopyrite. Thus in the latter case, of the pyrite- chalcopyrite couple, the chalcopyrite played the role of the anode its solubility rising to 170 times that of the one observed in the case of the pure chalcopyrite. It should be mentioned that the grains of the pure chalcopyrite fragment were coarser and the ore itself more compact, than those of the chalcopyritic pyrite sample and that the chalcopyrite was distributed in very fine granules in the pyrite. All these factors definitely contributed to the extraordinary increase of the solubility of the chalcopyrite touching the pyrite mentioned above.

Bornite usually contains chalcopyrite which is a product of dismixture, furthermore the so-called chalcopyrite flames — products of decomposition — can also always be detected in it. *Ramdohr*[10] established that dismixtured bornites containing chalcopyrite are extraordinarily sensitive resulting in the decay of the bornite portion of the ore being far more rapid in the course of the oxidation-cementation processes than that of the chalcopyrite laminae. If the potentials of chalcopyrite and bornite are examined in any solution (s. Tables) the potential of chalcopyrite is always more positive than that of bornite, i. e. the chalcopyrite plays the part of the cathode in the ore and the bornite that of the anode, hence in the course of the oxidation processes the latter will be the first to dissolve providing an explanation for the empirical fact described above. However, weathering oxidation processes cannot only be brought about by macro- and micro-cells like the two examples mentioned above, but also by galvanic pairs in which case the dimensions of one of the electrods may be below the limits of perceptibility as e. g. in the case of very finely distributed mechanical, or isomorphous impurities. Rosenkränzer has observed that the greater the iron content of a sphalerite the greater the extent of its solution. The sphalerites forming at high temperatures contain fairly large amounts of iron as the solubility of FeS in ZnS is of course in close relation with the temperature. In this case the sphalerite is anodic to the pyrrhotite of cathodic character its dissolution increases in proportion to the augmentation of its pyrrhotite content, i. e. the greater the amount of the component behaving as cathode the greater the solution.

In many polished sections prepared of apparently homogeneous ores it could be observed that the weathering and the oxidation begins and proceeds along the granule boundaries. The course of this process is visible during the electrolytic structure etching when the progress of the etching can be controlled under the microscope and photomicrographs can be made at the different stages.[4] On the three attached photomicrographs it can be seen that in the apparently quite homogeneous chalcocite of the polished sections the grain boundaries appear (Fig. 1). Later the dissolution becomes still more marked along the grain boundaries thus the latter get more definite (Fig. 2) and finally the corrosion of the grain surface (Fig. 3) also takes place. Galvanic cells, can namely not only be composed by ores having a different chemical composition but owing the the differences in potential of the boundary surface and the

core of the same ore as has been undoubtedly proved[11] through the micro-potential measurements carried out on metals and alloys a difference in the grain structure of the same ore is sufficient to initiate decomposition along the grain boundaries. In the cases when the grain boundary is

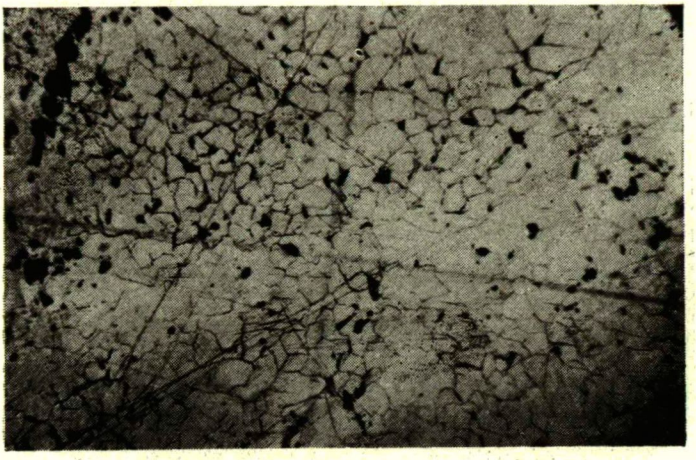


Fig. 1. Chalcocite, 70 ×

Fig. 2. Chalcocite, 90 ×

anodic to the cathodic core the decomposition starts at the grain boundaries, whereas in the reverse case the decomposition begins at the center of the grain. The effect of this type of heterogenity, however, is weaker from the point of view of the weathering than the electrochemical heterogenity which can be found in the case of systems consisting of different ores. In a system composed of two components the conditions seem rela-

tively simple. However, they become far more complex in the case of a system consisting of three, or even more ores. For our future investigations of these systems the theory of *Akimov*[12] concerning the polyelectrodic systems will afford a basis.

Fig. 3. Chalcocite, Oel imm. 400 ×

THE INFLUENCE EFFECTED BY THE CHANGES IN CONCENTRATION OF SINGLE IONS AND THEIR SOLUTIONS, ON THE ELECTRODE POTENTIALS OF SOME SULPHIDE ORES:

As has already been indicated the authors dealing with this problem in relation to the weathering of the ores laid great stress upon the environment and to the place they occupied in the electromotive force series. The question arises whether it can be assumed that in the case of the ores there is also a constant electromotive force series of a standard value similar to that of the metals, furthermore if for the interpretation of the oxidation processes such a series is really necessary.

On the basis of present opinion that presumably there is also a given electromotive force series for ores, the purpose of the investigation was to elucidate how the different ions, in the first place Cu^{++}, Fe^{++}, Fe^{+++}, Mn^{++}, Zn^{++} and the solutions of their sulphates varying in concentration influence this assumed electromotive force series, as well as the sequence of the minerals, i. e. what is the effect of the change of the sulphuric acid concentration as in the weathering of sulphide ores primarily sulphuric acid, sulphated solutions are involved.

For the investigation the following possibly pure homogeneous polished sections were chosen:
pyrite, pyrrhotite, chalcopyrite, bornite, covellite, chalcocite, enargite, tetrahedrite, galena, arsenopyrite, loellingite, niccolite, ullmannite, smaltine, safflorite.
Before beginning each series of measurements the surfaces of the polished sections were polished with the finest polishing powder (mean grain size $< 20\ \mu$) so that the quality of the surface of each ore should be identical

at all the measurements. A small glass bell into which an electrolyte was introduced was attached with bee wax to the surfaces of the ores after they had been polished and carefully cleaned. The end of the glass bell which was in contact with the ore was in every case identical in diameter (1 cm). Thus the same surfaces of the same size of all the ores came into contact with the electrolyte. As the perpendicular two opposite sides of the polished sections were polished parallel and fixed with a suitable forceps, a steady contact could be brought about. The measuring were carried out to a N calomel electrode having a compensator of 5 decade (10.000 Ohm resistance), as zero instrument a galvanic meter with a sensitivity of $7{,}65 \times 10^{-7}$ V/scale div., 22 Ohm resistance served. At the measurements the values were recorded 1 minute after the contact had been established. At all measuring the same polished sections were used the surface being cleaned before each measuring series as mentioned above. The values in the Tables are recorded in the N calomel scale and not recalculated for N Hydrogen electrode.

The measurements were carried out in 0.005, 0.010 0.050, 0.100 N H_2SO_4, 0.001, 0.010, 0.100 m $CuSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, $MnSO_4$, 0.1 m $ZnSO_4$ solutions and artificial mine inflow the composition of which was as follows: $CaSO_4 . 2H_2O$: 0.68 g, $Fe_2(SO_4)_3$: 1.15 g, $CuSO_4 . 5H_2O$: 4.47g, $MnSO_4 . 4H_2O$: 0.16 g, $ZnSO_4 . 7H_2O$: 0.23 g, $Na_2SO_4 . 10H_2O$: 0.40 g, $MgSO_4 . 7H_2O$: 1.47 g, H_2SO_4 : 2.98 g per liter. The different metal sulphate solutions corresponded to a solution of 0.05 N as defined in relation to sulphuric acid.

The results are summarised in the following Tables and Figures.

Table 1.

The changes of the electrode potentials depending upon the concentration of the sulphuric acid.

Ore	0,005 N	0.010 N	0.050 N	0.100 N
Pyrite	267 mV	273 mV	283 mV	287 mV
Tetrahedrite	219	218	219	219
Ullmannite	215	219	224	218
Covellite	211	206	203	194
Chalcopyrite	172	172	171	167
Enargite	161	159	161	161
Pyrrhotite	154	164	180	187
Bornite	138	135	124	121
Saffiorite	126	126	133	133
Chalcocite	115	113	103	93
Arsenopyrite	63	66	85	95
Galena	56	46	36	24
Loellingite	43	45	53	65
Smaltite	6	5	5	4
Niccolite	—14	—14	—14	—14

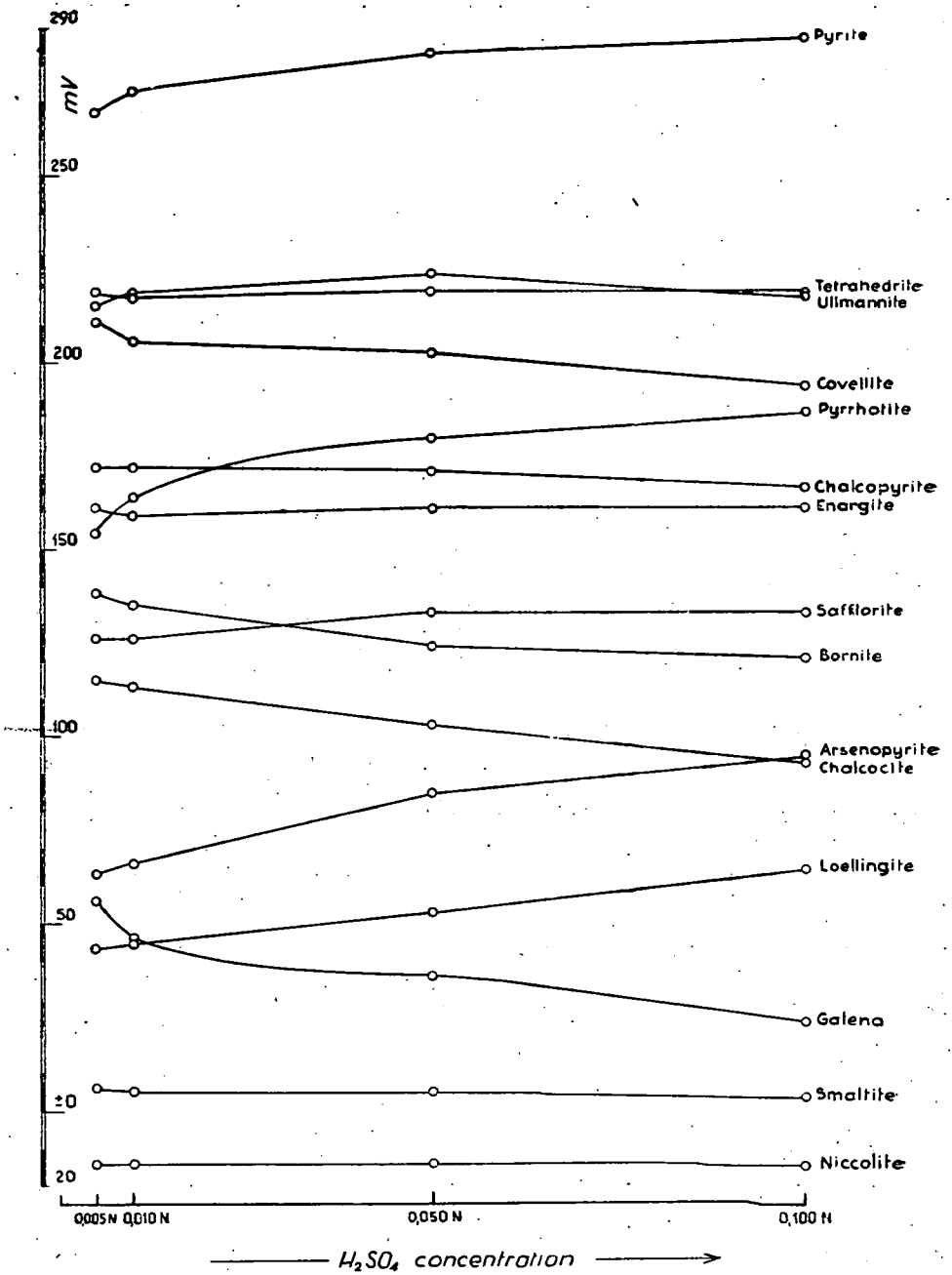

290
mV
250
200
150
100
50
±0
20
Pyrite
Tetrahedrite
Ullmannite
Covellite
Pyrrhotite
Chalcopyrite
Enargite
Safflorite
Bornite
Arsenopyrite
Chalcocite
Loellingite
Galena
Smaltite
Niccolite
0,005 N
0,010 N
0,050 N
0,100 N
H2SO4 concentration

Fig. 4.

Concerning the above data it should be mentioned that some of the measurings represent mean values. As the the reproducibility for the values under — 100 mV the deviation between the mean value and the single measurings is on the average ± 3 mV, in one case it is exceptionally ± 5 mV, for the higher values the deviation between the single measurements and the mean value is at the average ± 7 mV, not exceeding in any case ± 10 mV. Smaltine represents an exception considering that its potential changes very rapidly so that it could not be precisely measured by the described method, the reported value only corresponds to a very rough mean value though the order of magnitude and thus its place in the series can be safely stated.

Table 2.

Electrode potentials in a solution of 0.1 m $ZnSO_4$

Pyrite	274 mV	Safflorite	111 mV
Tetrahedrite	234	Chalcocite	96
Covellite	185	Arsenopyrite	74
Ullmannite	176	Loellingite	56
Chalcopyrite	157	Galena	35
Bornite	123	Smaltite	9
Enargite	118	Niccolite	—29
Pyrrhotite	112		

Table 3.

Electrode potentials in artificial mine inflow.

Pyrite	429 mV	Safflorite	207 mV
Enargite	425	Bornite	187
Ullmannite	324	Arsenopyrite	183
Chalcopyrite	348	Loellingite	158
Pyrrhotite	326	Chalcocite	143
Tetrahedrite	294	Smaltite	82
Covellite	282	Niccolite	77
Galena	239		

Table 4.

The changes of the electrode potentials depending upon the $FeSO_4$ concentration.

Ore	0.001 m	0.010 m	0.100 m
Pyrite	258 mV	255 mV	232 mV
Ullmannite	204	230	221
Covellite	191	191	194
Tetrahedrite	174	182	189

Ore	0.001 m	0.010 m	0.100 m
Pyrrhotite	160	178	182
Chalcopyrite	139	145	170
Bornite	124	124	118
Safflorite	123	133	132
Enargite	122	139	161
Chalcocite	104	99	95
Arsenopyrite	76	85	83
Galena	69	69	73
Loellingite	58	59	58
Smaltite	34	24	14
Niccolite	-26	-26	-38

Table 5.

The changes of the electrode potentials depending upon the $Fe_2(SO_4)_3$ concentration.

Ore	0.001 m	0.010 m	0.100 m
Enargite	337 mV	409 mV	440 mV
Pyrite	330	417	467
Tetrahedrite	267	324	382
Ullmannite	262	343	399
Chalcopyrite	251	350	414
Pyrrhotite	238	319	387
Covellite	203	277	405
Safflorite	157	214	319
Galena	155	225	310
Bornite	143	168	213
Chalcocite	115	127	169
Arsenopyrite	109	169	270
Loellingite	97	153	262
Smaltite	48	98	255
Niccolite	10	36	49

Table 6.

The changes of the electrode potentials depending upon the $MnSO_4$ concentration.

Ore	0.001 m	0.010 m	0.100 m
Pyrite	267 mV	265 mV	268 mV
Pyrrhotite	250	199	196
Enargite	237	216	210

Ore	0.001 m	0.010 m	0.100 m
Chalcopyrite	225	212	201
Ullmannite	216	223	224
Tetrahedrite	210	213	214
Galena	193	177	166
Covellite	192	195	192
Safflorite	132	133	128
Bornite	127	122	116
Chalcocite	125	117	102
Arsenopyrite	98	100	92
Loellingite	42	56	62
Smaltite	20	21	22
Niccolite	-15	-22	-26

Table 7.

The changes of the electrode potentials depending upon the $CuSO_4$ concentration.

Ore	0.001 m	0.010 m	0.100 m
Pyrite	264 mV	272 mV	280 mV
Ullmannite	222	243	257
Tetrahedrite	215	229	243
Pyrrhotite	214	215	230
Covellite	192	202	221
Chalcopyrite	182	199	225
Enargite	177	187	209
Galena	164	178	204
Bornite	162	168	194
Safflorite	131	141	150
Chalcocite	114	124	151
Arsenopyrite	106	119	135
Loellingite	82	90	108
Smaltite	41	50	63
Niccolite	23	34	53

THE EVALUATION OF THE ELECTROMOTIVE FORCE SERIES OF THE ORES

On the basis of his investigations *Rechenberg*[9] draws the following conclusions: the sequences of minerals is determined by the properties of their lattice structure, and influenced by their mechanical and/or isomorphous impurities. Furthermore, although the electrode potentials of the same minerals species originating from different deposits showed deviations of a centivolt in order of magnitude and the sequence also exhibited fluctuations, on the whole it was constant, i. e. the ore minerals

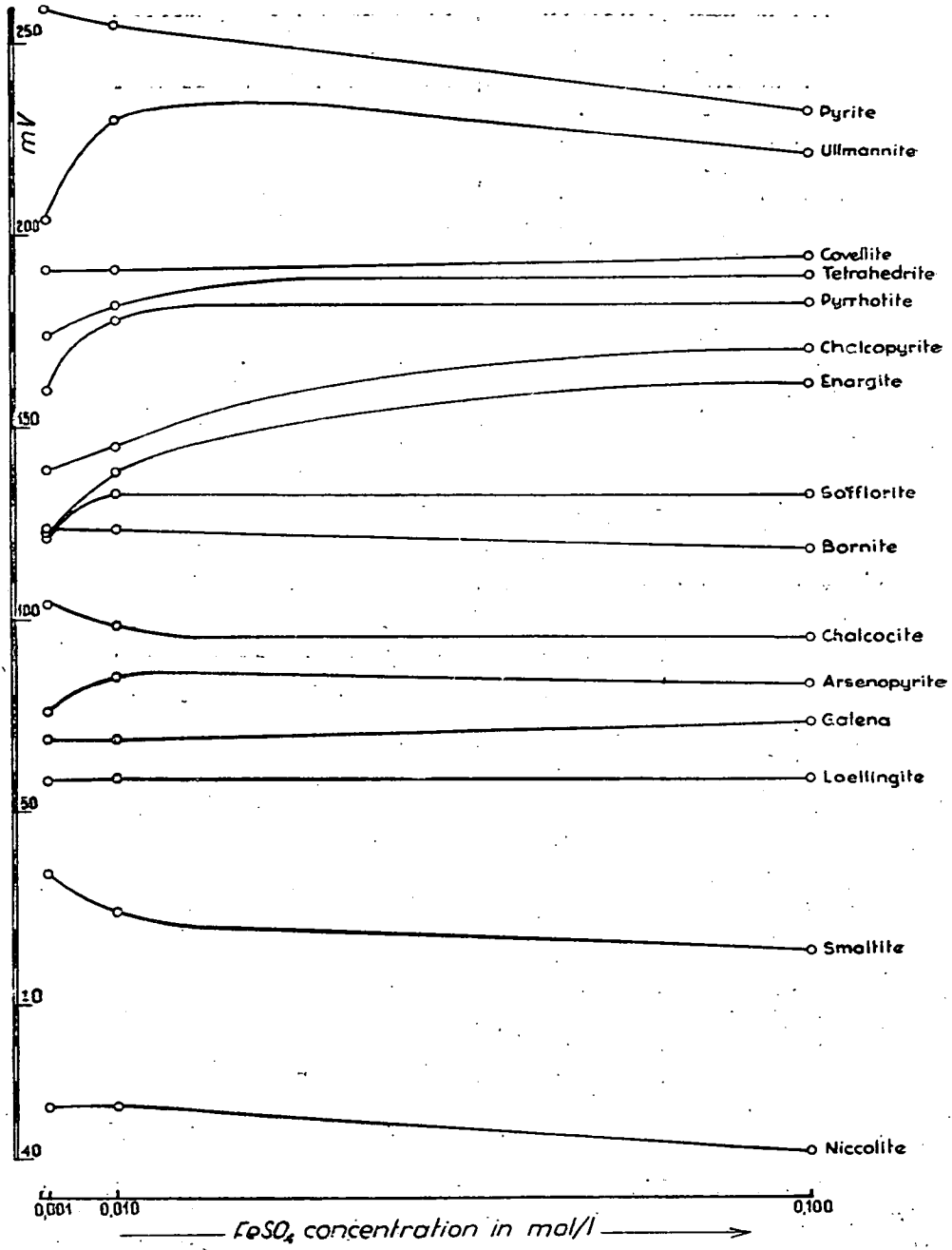

250
mV
200
150
100
50
20
40
Pyrite
Ullmannite
Covellite
Tetrahedrite
Pyrrhotite
Chalcopyrite
Enargite
Sofflorite
Bornite
Chalcocite
Arsenopyrite
Galena
Loellingite
Smaltite
Niccolite
0,001
0,010
0,100
FeSO4 concentration in mol/l

Fig. 5.

can be ranged into a certain electromotive force series. On discussing the examinations of the same author it was mentioned above that he recalculated his results for a N hydrogen electrode in order to obtain for the ores an analogous electromotive force series as that of the metals. As regards the above mentioned facts the following should be noted: in electrochemistry reversible electrode potentials correspond to the equlibrium potentials of a metal electrode and the ions of the same metal in a solution the concentration of which varies. Every reversible potential corresponds to a completely defined state of equilibrium which forms between the metal and its ions. If, therefore, the concentration of the metal own ions is increased at the electrode in the solution its electrode potential becomes more positive, if the solution is diluted it becomes more negative. The concentration of the metal ion in the solution corresponds to a definite electrode potential value. The potential which is derived to a N hydrogen electrode if the metal is immersed into a solution of a unite activity of its own ions at 1 atmospheric pressure and 25° C represents the N potential of the respective metal.

All these general establishments are only accentuated to show that if an electromotive force series of ores is mentioned and this is interpreted like that of the metals, i. e. an electromotive force series is regarded as the sequence formed from the N potentials, at the measuring of ores hitherto mentioned by various authors the sequences cannot be compared to the electromotive force series of the metals or still less considered to be analogous with them as the electrode potential values reported in the literature and in the present paper can by no means be identified with the N potentials of the ores. They cannot be considered to be the same, owing to the metal ions of the respective ore not participitating in unit activity in the solution, but also because in the case of most ores the ore is usually immersed into a solution not containing its own ions, but in one containing foreign ions. Under such conditions the ore cannot be considered to be a reversible electrode and the potential is not either an equilibrium potential. Whereas, just the latter case approaches reality the most closely, i. e. the cases when the ore comes into contact with solutions containing not only its own, but also foreign ions, or often predominantly only the latter.

Hence in the case of ores there does not exist an electromotive force series analogous to that of the metals. It is true that signes of a certain constancy can be detected in the sequence a fact which has already been reported by Rechenberg and is also confirmed by the present investigation. To give only a few examples and only considering the present results: the potential of pyrite is in all solutions the greatest, the smaltine — niccolite sequence does not either change in various solutions except in that of $Fe_2(SO_4)_3$ of 0.1 mol when the electrode potential of smaltine increases to a great extent and that but for this one case the electrode potentials of both are at the end of the sequence; the of bornite-chalcocite or that of arsenopyrite-loellingite do not either change. In the copper ore series chalcopyrite and covellite had always more positive electrode potentials than bornite or chalcocite.

However, in the solutions of the different ions the concentration of which varied the sequence of the electrode potentials of ores showed a

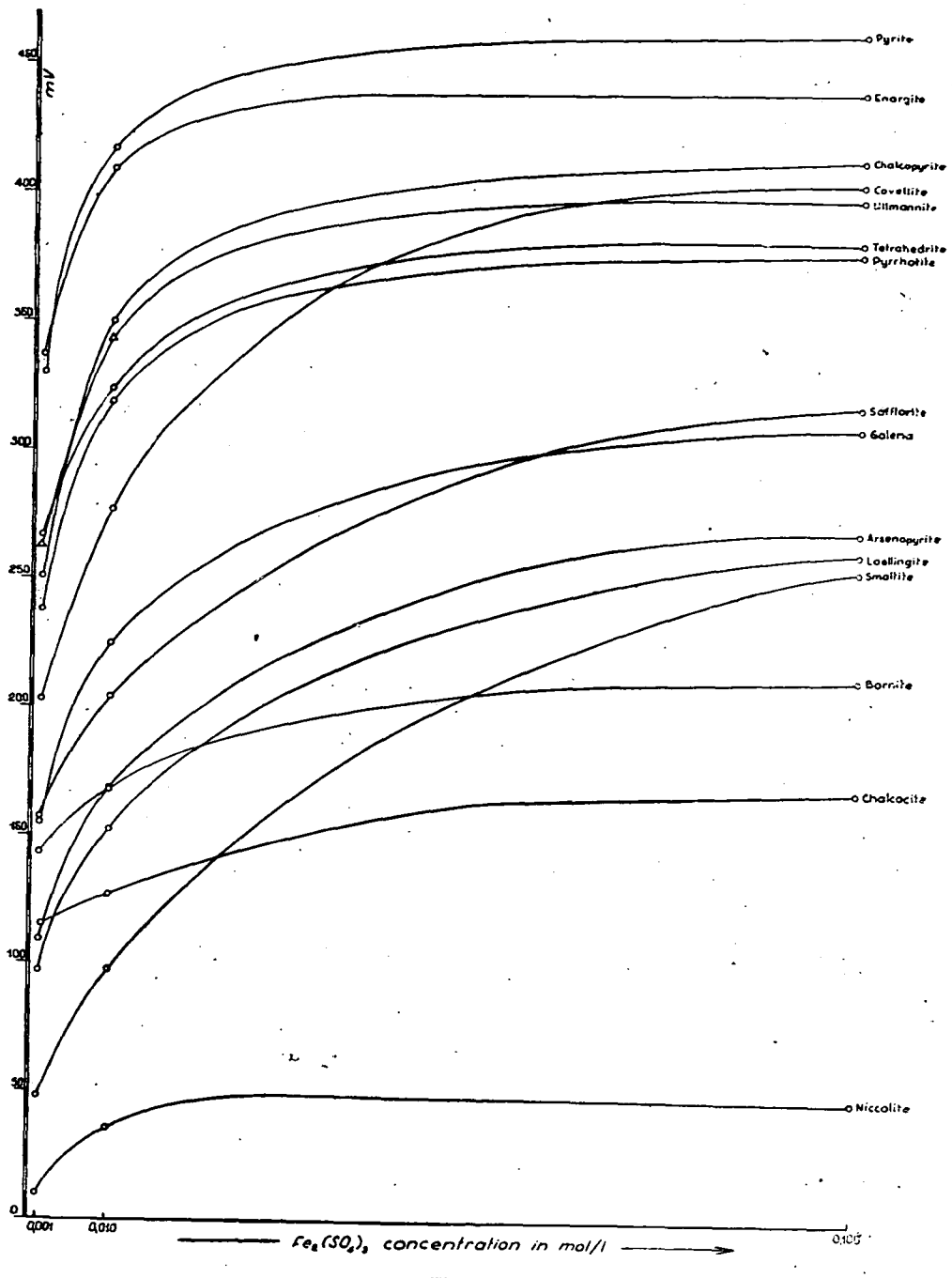

mV
450
400
350
300
250
200
150
100
50
0
0,001
0,010
0,100
$Fe_2(SO_4)_3$ concentration in mol/l
Pyrite
Enargite
Chalcopyrite
Covellite
Ullmannite
Tetrahedrite
Pyrrhotite
Safflorite
Galena
Arsenopyrite
Loellingite
Smaltite
Bornite
Chalcocite
Niccolite

Fig. 6.

very marked change (s. Figs.) which seems to be in contrast with the assumption of the existence of a permanent sequence, although in our opinion this fact is not very essential. Whether or not there exists a constant sequence which is generally valid is all the less important considering that the electromotive force series is only a basis to deduce conclusions by virtue of the place of the ore in the series as to e. g. which of two ores will play the role of the cathode and which that of the anode, i. e. which will be oxidised on coming into contact with a certain electrolyte. As can be seen from the measurements when the composition of the solution changes not only the value of the different electrode potentials changes, but also the sequence itself, sometimes even to a great extent. Presumably in the case of ore lodes the conditions are considerably complex not only because they frequently represent polyelectrodic systems with many components, but also because in addition to the composition of the ore lodes being able to undergo changes from top to bottom, the composition of the electrolyte itself, that of the mine inflow, may change and indeed changes. Furthermore, even if the average composition of the ore body and that of the mine inflow remain the same there can still occur differences in the oxygen content of the mine inflow touching the upper zones and the deeper levels of the ore lode, which difference, in itself is enough to cause weathering, oxidising processes.

Hence as regards the weathering of the sulphide ores the establishment in the closer sense of the word of the electromotive force series based on that of the normal potentials is not an essential factor, the more so since hitherto such messuring results were not available. For instance on considering the electromotive force series of metals it is revealed that the normal potential of zinc is —0.762, that of aluminum —1.67, thus in the case of a galvanic couple consisting of the two metals by virtue of their place in the electromotive force series aluminum ought to dissolve, whereas in a solution of N sodium chloride just the contrary occurs, the potential of the zinc measured to a 0.1 N calomel electrode is —1 and that of aluminum —0.85.[11] It may therefore be stated that also in the case of ores the normal electromotive force series is not essential, what is important is what potentials result for certain ores in a given electrolyte and what for a sequence will thus be created. This also supports the assumption which we have already suggested a few years ago that at the interpretation of the weathering and oxidation conditions of a mining district it should not be attempted establish the electromotive force series of the ores in general by determining their normal potentials, but that such investigations should deal with each respective mining district individually taking the mineral associations, the impurities contained in the minerals and the composition of the solutions influencing the mining districts — the active factors primarily influencing the electrode potentials of the ores — into considerations.

If the point of view stated above are actually realised we can still only interpret the mineral association of a mining district qualitatively concerning its oxidation conditions. To interpret also quantitatively the oxidation processes of polyelectrodic systems consisting of different ores even the most precise measurements of the electrode potentials of the given ores in a solution of a determined composition is not sufficient.

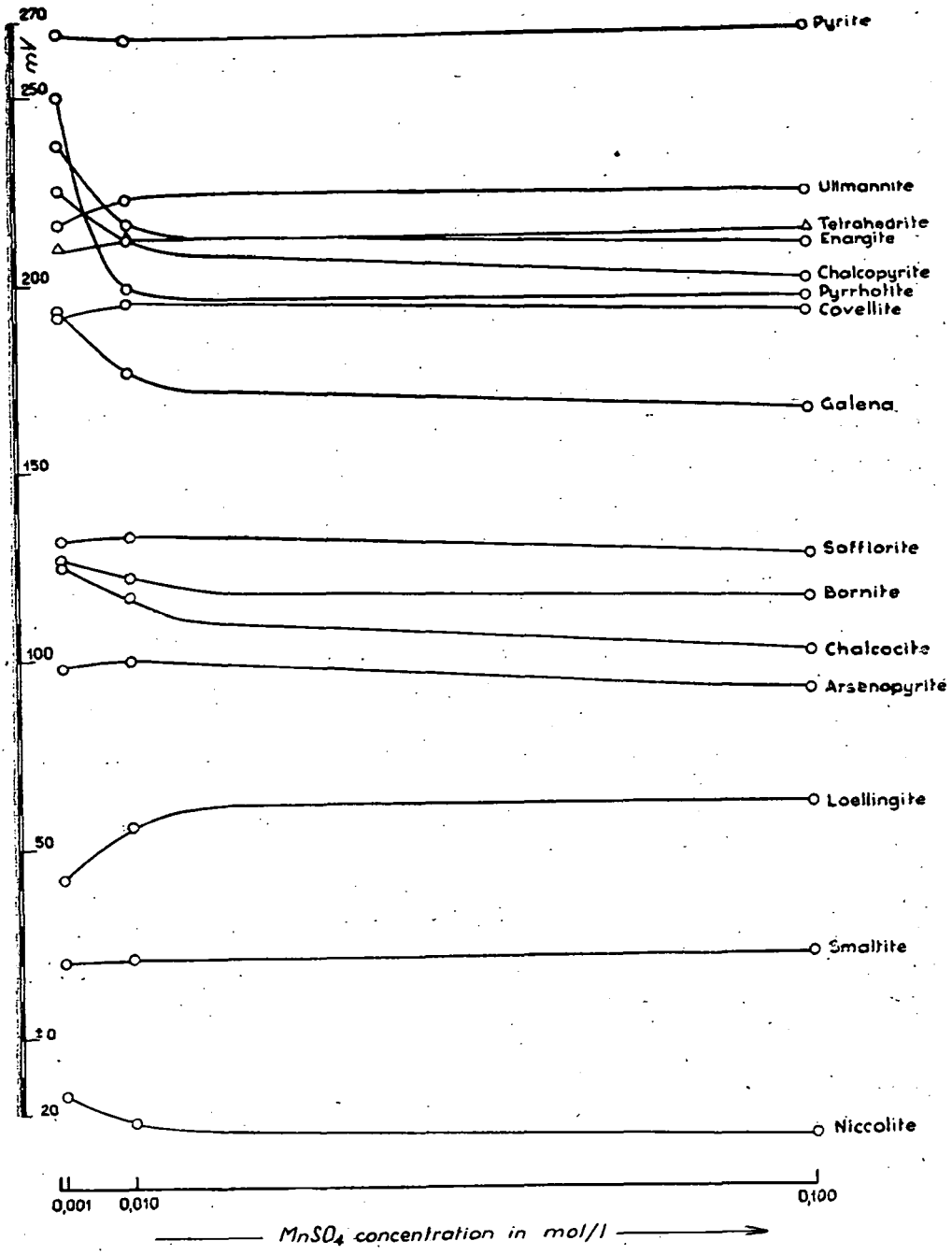

270
mV
250
200
150
100
50
±0
20
Pyrite
Ullmannite
Tetrahedrite
Enargite
Chalcopyrite
Pyrrhotite
Covellite
Galena
Safflorite
Bornite
Chalcocite
Arsenopyrite
Loellingite
Smaltite
Niccolite
0,001
0,010
0,100
MnSO4 concentration in mol/l

Fig. 7.

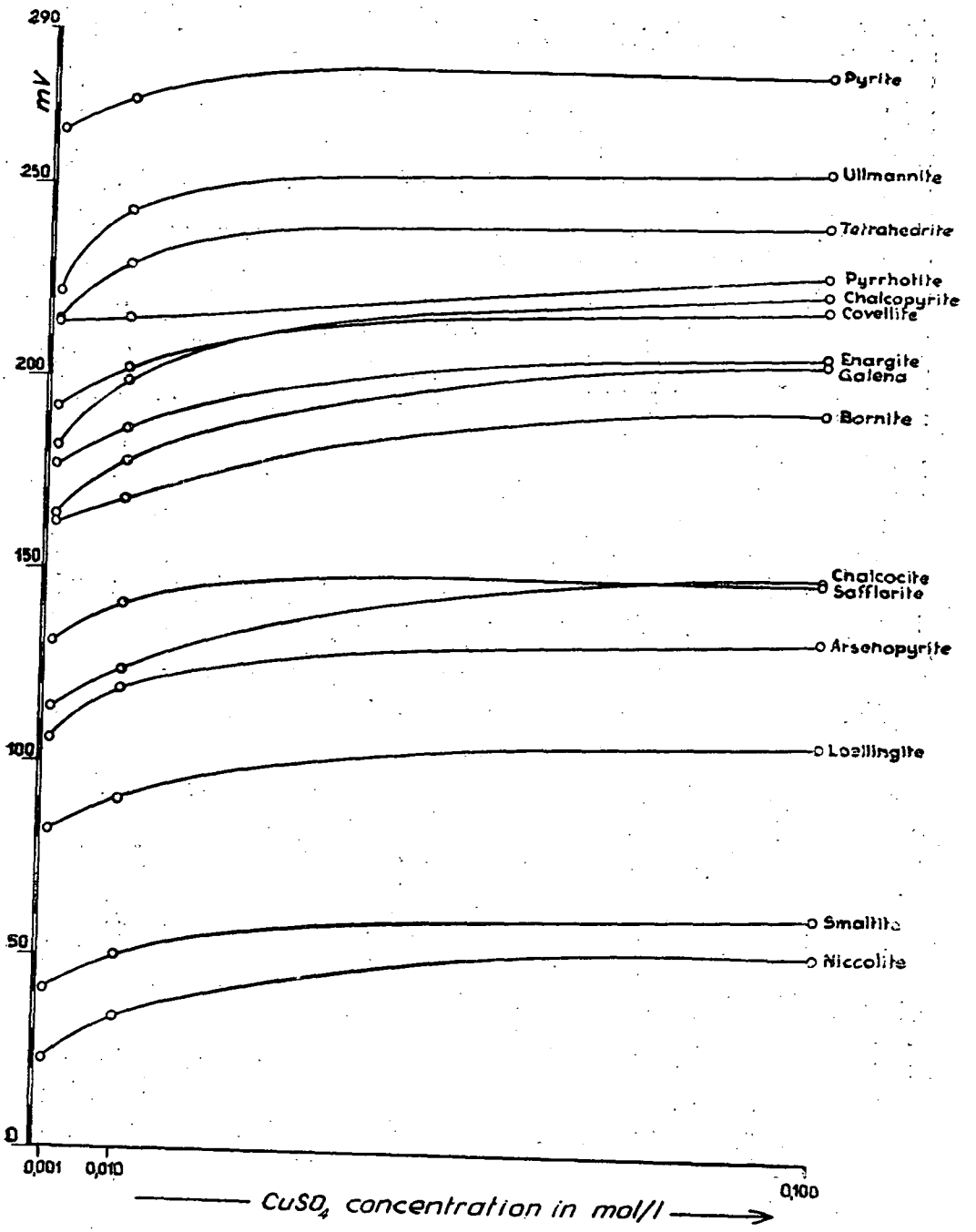

290
mV
250
200
150
100
50
0
Pyrite
Ullmannite
Tetrahedrite
Pyrrhotite
Chalcopyrite
Covellite
Enargite
Galena
Bornite
Chalcocite
Safflorite
Arsenopyrite
Loellingite
Smaltite
Niccolite
0,001
0,010
0,100
CuSO4 concentration in mol/l

Fig. 8.

As even on the basis of the most precisely established electromotive force series the magnitude of the change and of the dissolution of the anodic ore, as well as the extent of its oxidation cannot be derived. It is true that the electromotive force series, particularly in the case of simple systems with two components, render it possible to ascertain that in a given solution which of the two ores will be the anode and which the cathode, as the potential difference between the two ores is a measure of the driving force tending to cause corrosion currents, but the magnitude of these currents is the only true measure of the velocity of the galvanic attacks. If two ores the electrode potentials of wich are known compose a couple in a solution of given composition the electrode potential of the cathode and the anode, as well as the potential difference between the two only relates to the initial period of the functionning of the couple and these values soon change, thus as already mentioned, the rate of the weathering process is not in correlation with the initial potential difference of the two ores. Hence our investigations in progress deal with the changes of the electrode potentials of different ores related to time in a known solution, i. e. the cathodic and anodic polarizations and the change of the current magnitude related to time in systems with two or more components.

Acknowledgement.

I am very obliged to *Mr. M. Solti* who helped me with his advice and by making available to me his paper[13] not yet published.

REFERENCES:

1. Koch—Grasselly: Processes Occurring at the Decomposition of Sulphide Ores. Acta Mineralogica Petrographica Tomus V. 1951.
2. Koch—Grasselly: Data on the Oxidation of Sulphide Ore Deposites. Acta Mineralogica Petrographica Tomus VI. 1952.
3. Grasselly: Qualitative chemische Untersuchungen an sulfidischen Erzanschliffen. Acta Geologica Academiae Scientiarum Hungaricae, Tom. I. 1952.
4. Grasselly: Electrographical Analysis of Ore Textures. Acta Mineralogica Petrographica Tomus VI. 1952.
5. Gottschalk—Buehler: Oxidation of Sulphides. Econ. Geol. 5. 1910.
6. Wells: Electrochemical activity between solution and ore. Econ. Geol. 8. 1913.
7. Wells: Electric activity in ore deposites. U. S. Geol. Survey Bull. 548. 1914.
8. Rosenkränzer: Über die Geschwindigkeit der Auflösung von Bleiglanz und Zinkblende in verd. H_2SO_4. Z. f. anorg. Chem. Bd. 87. 1914.
9. Rechenberg: Untersuchungen über die elektrochemische Spannungsreihe der Erzmineralien. Neues Jahrbuch f. Min. Monatshefte, Jahrg. 1951.
10. Ramdohr: Lehrburch, der Erzmikroskopie. Bd. II. 1931.
11. Mears—Brown: Causes of Corrosion Currents. Ind. and Eng. Chemistry. Vol. 33. 1941.
12. Akimov: Fémek korróziójának elmélete és vizsgálatának módszerei. Nehézipari Könyvkiadó 1951.
13. Solti: A potenciálmérés mint korrózis vizsgálati módszer kritikája. (Not yef published.).

JAROSITE FROM MOUNT GÉCSI

(The Mountain Range of Velence)

BY J. ERDÉLYI AND V. TOLNAI

The Board of Directors of the Hungarian Geological Institute expressed in 1952 the wish that we should examine the yellow coloured unknown mineral samples originating from the collection of B. Jantsky. The mineral samples were found at the investigations carried out in the Mountain Ranges of Velence at Mount Gécsi. The results of the investigation are as follows:

The granite mother rocks contained radial crystal prints. These »radial minerals« are the prints of some primary mineral, the walls of these prints are coated with yellow coloured glittering small crystals 1—2 tenth of a mm in size, or even still smaller, obviously they are perimorphs. At the first glance these glittering crystals seem to be a combination of hexahedrons and tetrahedrons. Their hardness is very slight: 2—3. They dissolve in warm HCl. The solution contains considerable amounts of iron and sulphate. If the mineral granule is moistened with HCl it shows a bright sodium- and potassium flame reaction. When heated in a test tube it gives off water. On heating in a closed test tube with Mg splitters till it shows a thin metallic As mirror and sulphur sublimation forms. This indicates that it is potassium-sodium-iron sulphate containing water.

The very small dimensions of the minute crystals render angular measurements with instruments very difficult. However, we after all succeeded in measuring the angle of inclination of the would be hexahedron and tetrahedron planes on a small crystal: it was 55°.

According to the so far gathered data it seemed likely that the mineral is jarosite the chemical composition of which is $KFe_3(SO_4)_2 \cdot (OH)_6$. The crystal shape of jarosite is a combination of a rhombohedron approaching closely a hexahedron and that of the basal plane. The angle of the rhombohedron is 90° 45′. The angle of inclination of the basal plane and the rhombohedron plane is:

$$c(0001) : r(10\bar{1}1) = 55° 15'$$

These data are in good agreement with our observations and the angle measurements mentioned previously. The hardness, lustre and colour of the jarosite also corresponds with the above data.

To obtain definite data the chemical laboratory of the Geological Institute analysed the mineral chemically. The analyses were made by V. Tolnai and Mrs. Földvári. The results of the analyses were published in a letter by the Board of Directors of the Geological Institute on January 28, 1953. The data of the analyses are as follows:

Insoluble in HCl	27.44 %
$-H_2O$	0.39
$+H_2O$	7.93
Fe_2O_3	31.69
Al_2O_3	3.98
SO_3	22.45
K_2O	5.46
Na_2O	1.07
	100.40 %

The examination of the part wich is insoluble in HCl:

SiO_2	76.56 %
Al_2O_3	14.70
Fe_2O_3	0.93
TiO_2	traces
CaO	0.61
MgO	1.28

Spectroscopical investigation:

Main mass: Fe, Na, K, Al, Si.

Pronounced traces: As

traces: Pb

Very slight traces: Ag

From the point of view of the mineral examination the data relating to the part insoluble in HCl are the decisive ones. Therefore, by increasing the analytical data of the part is soluble in HCl with 27.44 per cent which corresponds to the insoluble part, the analytical data were supplemented to 100.40 per cent. After the recalculation the analytical data are as follows:

H_2O (entire water)	11.45 %
Fe_2O_3	43.61
Al_2O_3	5.48
SO_3	30.89
K_2O	7.51
Na_2O	1.47
	100.41 %

The corresponding molecule quotients are:

H_2O	0.63557	~	6
Fe_2O_3	0.27311	0.32673	~3
Al_2O_3	0.05362		
SO_3	0.38579	~	4
K_2O	0.07972	0.10889	=1
Na_2O	0.02917		

Considering that Al can substitute the Fe and sodium the potassium the mol-quotients of Al and Fe and those of potassium and sodium were summated. Hence the formula of the mineral is:

$$K_2O \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O = KFe_3(SO_4)_2(OH)_6,$$

which corresponds exactly with the chemical composition of jarosite. Considering that sodium jarosite, argentojarosite and plumbojarosite are well known minerals and that Al often substitues Fe in jarosite, furthermore that in the case of complete substitution the chemical composition of alunite is obtained: $KAl_3(SO_4)_2(OH)_6$, the minerals found in Mount Gécsi can be considered to be a mixture of the above minerals. The mineral mixture resembling the latter which also mostly contains carphosiderite (cyprusite) occurring usually in earthy aggregates as incrustations, is termed by the miners »yellow iron ore« or »misy«. The data of the analysis have revealed that as regards the examination of the mineral the part which is insoluble in HCl is of no importence. The main bulk of this insoluble part is aluminum silicate an impurity originating from the silicate of the granite rocks which mingled with the substance under investigations as the jarosite was scraped off from the mother rocks. However, if they are dissolved in HCl the two substances can be completely separated.

Jarosite is a secondary mineral forming at the decomposition of sulphide iron ores in a dry atmosphere. It is the characteristic mineral of »iron hat«. Limonite is another decomposition product which can be found in small globules associated with the jarosite of Mount Gécsi. Considering that alunite occurs at many places in the Mountain Range of Velence as a result of the action of »solfatara« the presence of alunite associated with jarosite is not surprising.

The primary sulphide minerals were most probably radial marcasite and in the main bulk radial arsenopyrite this assumption is confirmed by the As impurity contained in them. This also explains the radial mineral prints on the walls of wich the small jarosite crystals are deposited. The Ag and Pb traces are probably due to the impurities contained in the primary ore, or in its associated minerals.

National Museum for Natural Sciences, Min. Dept. Budapest.

VORKOMMEN VON FLUORIT BEI LEVICE

A. VENDL

In einem Hohlraum des Travertins SO von Levice (Tschechoslowakei) wurden zwei aufgewachsene, farblose vollkommen wasserklare Kristalle von Fluorit festgestellt. Die Kristalle bilden ideal ausgebildete Hexaeder; Kantenlänge 10 mm, resp. 6 mm. Der Fluorit scheint hier ein seltenes Mineral zu sein.

FLUORIT ELŐFORDULÁSA LÉVA (LEVICE) MELLETT

VENDL ALADÁR

A Léva (Levice) városától DK-re levő triász terület forrásmészkövét *Koch Sándor* ismertette.[1] A terület földtani viszonyait *Ivan Ludovit* foglalta össze.[2] A forrásmészkő mintegy közel 2 kilométeres körzetben ismert és két nagyobb — több kisebb fejtésből összetevődő — kőbánya tárja fel.

A területet 1941 nyarán *Papp Ferenc* professzor társaságában tanulmányoztam.

A déli nagy kőbányában az egyik kifejtett forrásmészkőtömb egyik kis üregében *fluoritot* találtam. Az üregben két fluorit-kristály ült az üreg falán. Mind a két kristály ideálisan kifejlődött kocka; az élhossza 10 mm, a másiké 6 mm volt. A színtelen víztiszta, üvegfényű kristályok egyik lapjukkal voltak az üreg falára nőve.

Úgy látszik, hogy a fluorit itt ritka. A két kristályon kívül szorgos kereséssel sem sikerült többet észlelni.

University of Technical Sciences, Min. Geol. Inst. Budapest.

[1] Koch Sándor: Egyetlen magyar diszítőkövünk, a lévai onixmárvány. Természettudományi Közlöny, 72, 1940, p. 173—175.

Koch Sándor: A lévai (Levice. Csehszlovákia) és korondi (Corund, Románia) forráskövek. Acta mineralogica, petrographica, tomus III., p. 17—29. Szeged, 1949.

[2] Ivan Ludovit: Geologická stavba a minerálne pramene okolia Levic. Geologické práce; sosit 32. Slovenská Akadémia Vied a Umeni, Bratislava, 1952, p. 221(5)—233(17).

INDEX

INDEX

Megjelent 250 példányban
Felelős kiadó: Koch Sándor

Csongrádmegyei Nyomdaipari V. (H) 54-5404 — Felelős vezető: Vincze György